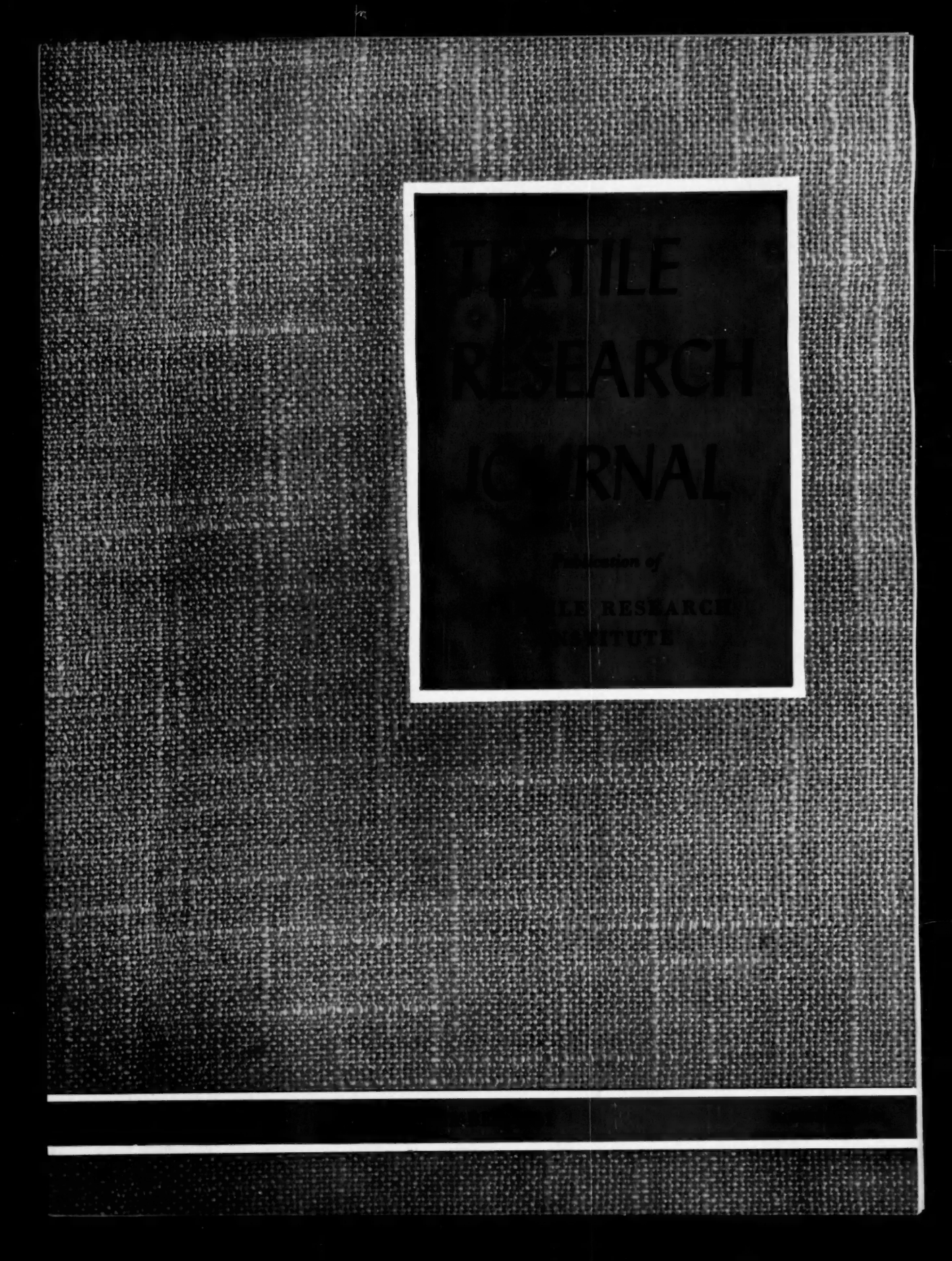

TEXTILE
RESEARCH
JOURNAL
Publication of

One of a series

COOKIES & CO_2 & CORDUROY

were the ingredients of this unlikely mystery. Stains on the pastel shades started it. The finisher blamed the dyer, the dyer blamed the bleacher, the bleacher said oil on the knives did it, and the boss weaver put the finger on the chemist. He couldn't find a patsy—until he found that the spotted goods had all gone through the number three treadle-brush. When the machine checked out clean, he set one of his men to play Pinkerton on the operator.

That's when the real story came out: the oldtimer on the brush didn't have a tooth in his head—but he loved cookies with his lunch. Being without dentures, he had to take a swig of "tonic" to soften every mouthful. Unfortunately, the soda pop was sometimes warm and the CO_2 pressure was just too much for him—so the pinwale going through the machine at noon got a spray of cookies-in-coke. (The problem was solved once for all by the personnel man and a local dentist.)

All this, of course, leads up to the commercial: did you know that the name Wallerstein means as much to bakers and bottlers as to textile people? Wallerstein enzymes and dough conditioners help put the "good" into baked goods today—and Wallerstein antioxidants help preserve the fresh fizzy flavor of packaged soft drinks. Think about that at lunch time. Think about this too: constant searching for better food additives fills our shelves with many experimental, development and commercial enzymes. Many types. Many grades (from AR on down). It's possible that one of these enzymes can solve a sticky problem in textile research or production. Maybe even the one you are working on right now. You ought to write us if you think we can help. (And remember, please, we make Rapidase® and Serizyme® too.)

WALLERSTEIN COMPANY
Division of Baxter Laboratories, Inc.
Staten Island 3, N. Y.

Need a High Potency Cellulase? Write Dept. R-11.

TEXTILE RESEARCH JOURNAL

Volume 31 — *November 1961* — Number 11

Editor:
Richard K. Toner

Production Editor:
Dorothy Dana Hollmann

Advisory Board

Herbert J. Ball
Earl E. Berkley
John Boulton
C. H. Fisher
Walter J. Hamburger
Milton Harris
R. M. Hoffman
Harold P. Lundgren
Herman Mark
George Switlyk
Helmut Zahn

TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is published by Textile Research Institute.

Manuscripts and communications should be sent to the Publications Department, P.O. Box 625, Princeton, N. J.

Second-class postage paid at Lancaster, Pa.

Subscription rates: $25.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Single copies, $2.50 each.

Contents copyright © 1961 by Textile Research Institute. Advertising rates supplied on request.

IN THIS ISSUE

The Effect of Radial Heterogeneity on Fiber Properties. *R. W. Singleton and M. A. Sieminski* 917

Theoretical Aspects of Hook Removal at Drafting Operations. *V. B. Merchant* 925

Some Studies on the Formation of Hooks in Carding. *V. A. Wakankar, S. N. Bhaduri, B. R. Ramaswamy, and G. C. Ghosh* 931

The Use of Coreactant Curing Agents with a Diepoxide to Impart Wrinkle Resistance to Cotton Fabrics. *Robert M. Reinhardt, Russell M. H. Kullman, Harry B. Moore, and J. David Reid* 941

Studies on the Chlorine Retention of Fabrics Treated with Dimethylol Ethylene Urea. *P. C. Mehta and J. R. Mody* 951

The Physical Properties of Wool Fibers at Various Regains. Part IV: Mechanical Changes Due to "Incorporated" Water. *M. Feughelman and I. C. Watt* 962

Part V: The Nature of Birefringence. *A. R. Haly and O. A. Swanepoel* 966

Relaxation Shrinkage of Wool Fabrics: Its Occurrence in Worsteds and Dependence upon Cloth Structure. *K. Baird* 972

The Accelerotor as a Test Machine for Felting Shrinkage. *G. L. Stott* 977

LETTERS TO THE EDITOR

A Preliminary Study of a Technique for Measuring Flexural Vibrations in Fabrics. *J. W. S. Hearle and D. J. Turner* 981

Observations on the State of Supercontracted Wool. *A. R. Haly and J. W. Snaith* 986

Graft Polymers of Cotton Cellulose and Acrylonitrile Initiated by Radiation. *Jett C. Arthur, Jr. and Robert J. Demint* . 988

Some Aspects of the Reaction between Urea and Cellulose. *A. C. Nuessle* 990

Concerning Some Aspects of the Reaction between Urea and Cellulose. *Leon Segal and F. V. Eggerton* 991

A Mechanical Model to Represent the Viscoelastic Properties of Polypropylene. *Henry M. Morgan and Roy C. Laible* 993

An X-Ray Study of Partially Hydroxyethylated Cellulose. *R. St. John Manley* 995

IN THE DECEMBER ISSUE .....inside back cover

REPRINT REQUESTS SHOULD BE DIRECTED TO THE AUTHORS
SEE ARTICLES FOR ADDRESSES

TEXTILE TECHNICAL

Development and Liaison Officer

FOR JAPAN

The International Wool Secretariat invites applications for the post of Technical Officer in its Japanese Branch, Tokyo.

The International Wool Secretariat is an organization established by the statutory Wool Boards of Australia, New Zealand and South Africa for carrying out their global policy of increasing the consumption of wool by means of promotion, market research, scientific research, technical development and liaison with all segments of the wool consuming and distributing industries.

Applicants should have a degree in chemistry, physics, chemical or mechanical engineering or the equivalent as well as several years' experience in either research, development or production in the textile industry. Such experience in the various branches of the wool textile industry would be an advantage.

Fluency in speaking Japanese and reading Japanese professional publications is essential. The duties of the Technical Officer will include organizing a technical information and service group to introduce into the Japanese wool textile industry new techniques (chemical and physical) for producing new and improved wool products and for increasing the efficiency of wool manufacturing. The Technical Officer will be required to maintain close contact in English with similar I. W. S. operating groups throughout the world.

Remuneration will compare favorably with similar appointments in Japan.

Applicants should apply in writing giving full details of their qualifications and personal background to:

Director of Science and Technology
The Wool Bureau, Inc.
360 Lexington Ave., New York 17, N. Y.

WASH & WEAR

Crease Resistance

by

acidifying Glyoxal solutions with

GLYOXYLIC ACID 40% Solution

acting as catalyst, with combined acid-aldehyde function.

The acid condensates with the fiber by formation of acetal at pH_3 to pH_4.

GLYOXYLIC ACID

Now available in tonnage quantities

DR. F. JONAS COMPANY
55 West 42nd Street New York 36, N. Y.

Technical Director

required for textile research center. The work of these laboratories is the main background of a well established commercial business and is concerned with sales service and development and evaluation of spin finish for synthetics, worsted oils, non-soiling lubricants, detergents, resin finishes, new textile finishing processes, etc.

The well equipped laboratories are staffed with highly qualified personnel and offer congenial surroundings, scientific atmosphere, cooperative research with other laboratories. Special consideration given to degree of experience in practical textile processing and ability to get along with people. Ph.D. preferred, but initiative, accomplishment, and leadership factors will weigh as heavily as academic standing.

Encouragement for original research work in application field and for cooperation with central group engaged in basic research in field of fatty chemistry. Our employees are aware of this advertisement. Reply to Box D36, TEXTILE RESEARCH JOURNAL, Princeton, N. J.

NOVEMBER 1961
VOL. 31 NO. 11

TEXTILE RESEARCH JOURNAL

The Effect of Radial Heterogeneity on Fiber Properties[1]

R. W. Singleton, M. A. Sieminski, and B. S. Sprague

Summit Research Laboratories, Celanese Corporation of America, Summit, N. J.

RADIAL heterogeneity or the presence of a skin has been demonstrated in many fibers. For example, Chamberlain and Khera [4] have shown differences in the radial structure of viscose and cuprammonium rayons. Peck and Kaye [7], and Scott and Ferguson [8] have demonstrated skin–core structure in acetate and polyacrylonitrile fibers while Waters [9] has revealed this phenomenon in Dacron.[2]

The presence of radial heterogeneity is usually ascribed to differences in the rate of radial coagulation of a fiber during spinning. As the fiber is extruded from the jet, the surface is preferentially coagulated by solvent flashing in dry spinning, rapid surface cooling in melt spinning, and surface precipitation in wet spinning. In wet and dry spinning, the coagulation then proceeds radially at some rate defined by solvent diffusion out or precipitant diffusion into the center of the fiber. In melt spinning, the rate of radial coagulation depends on the heat transfer from the fiber to the surrounding atmosphere.

In all three cases, during coagulation, viscosity gradients exist radially in the fiber which, in turn, cause shear gradients during drawdown. Hence, as shown schematically in Figure 1, radial coagulation results in heterogeneity of molecular orientation, with the greatest orientation at the surface of the fiber and diminishing orientation toward the fiber center.

The effect of such a nonhomogeneous structure on resulting fiber properties is of considerable interest to fiber manufacturers. It has already been demonstrated by Morehead and Sisson [6] that the surface, or skin, structure of viscose rayon exhibits different dyeing characteristics than the core structure, while Chamberlain and Khera have shown the effect of radial heterogeneity on mechanical properties of viscose [4]. It is the general opinion of those working with viscose that the effects attributable to the skin are due to differences in crystallinity rather than molecular orientation [6].

Unfortunately, there is a dearth of information concerning the mechanical properties and dyeability characteristics resulting from radial heterogeneity in other fibers. It is the purpose of this paper to detect the presence of skin–core structure in a model fiber, to relate this heterogeneous structure to the conditions of fiber coagulation, to speculate on the nature of the radial heterogeneity, and to determine its effects on the mechanical and dyeing properties of the fiber.

Materials and Methods

Cellulose triacetate (CTA) is particularly advantageous as a model polymer for this work since a wide variety of coagulation conditions favoring either radial homogeneity or heterogeneity can be utilized for fiber preparation. Furthermore, fibers produced over this range of conditions exhibit essentially no

[1] Presented at the Thirty-first Annual Meeting of Textile Research Institute, New York City, March 16–17, 1961.

[2] Du Pont polyester fiber.

crystallinity in the absence of heat treatment, as shown by their X-ray diagrams depicted in Figure 2. Hence, any effects of skin–core structure on fiber properties can be attributed to other fine-structure characteristics.

With cellulose triacetate, a simple technique can be used to remove known thicknesses of outer surface for the purpose of studying the properties of the remaining fiber.

Chamberlain and Khera [4] removed surface layers of varying thickness from viscose by heterogeneous acetylation followed by dissolution of the cellulose acetate layer with a suitable solvent. The technique utilized in this study is essentially the reverse, i.e., saponification of the triacetate fiber surface in alkali followed by a treatment with a solvent to dissolve the cellulose layer. This technique cannot be used with secondary acetate since the saponification treatment causes swelling, hence, alteration of the remaining fiber structure. However, with triacetate, it will be shown that saponification proceeds progressively, layer by layer, from the surface.

It was anticipated that dry spinning of CTA would favor the creation of a model fiber with skin–core structure due to high rate of initial solvent evaporation.[3] A variety of spinning conditions are capable of producing this effect, and the following simple method, described in the literature [1, 3, 5], was utilized. CTA polymer was spun from a 90/10 methylene chloride/methanol solution into hot air. The temperature of the air into which the filaments were extruded was maintained at a temperature above the boiling point of the solvent in order to ensure solvent flash-off at the surface of the dope stream, thus causing rapid surface coagulation. The remainder of the dope coagulates more slowly by a process involving the diffusion of solvent to the fiber surface where it can then be flashed off. It is fairly obvious that the relative rates of surface and core coagulation can be affected by such spinning parameters as air temperature, spinning speed, solvent system, and solvent concentration.

[3] It should not be inferred that all dry spun fibers will have skin–core structures, while all wet spun fibers will be radially homogeneous. Sufficient alteration of the coagulation conditions in either type of spinning will allow the production of radially homogeneous or heterogeneous fibers.

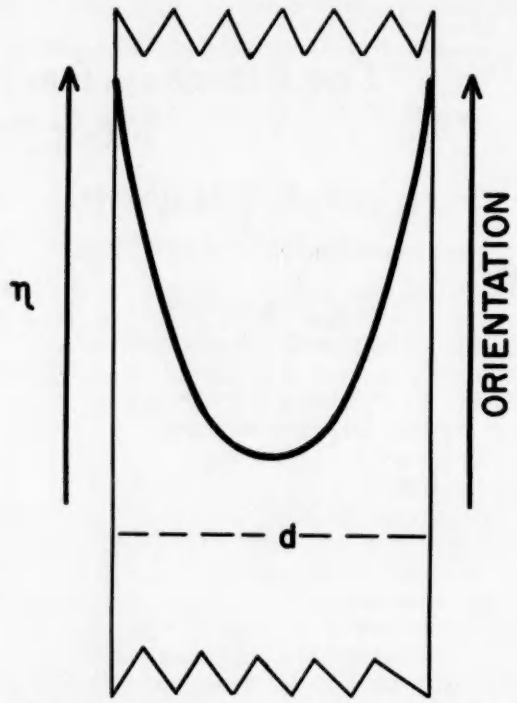


Fig. 1. Relationships of viscosity gradient and orientation to fiber diameter during coaguiation of fibers exhibiting skin–core structure.

Fig. 2. X-ray diagrams of CTA fibers from fast and slow coagulation systems. Left, hot air rapid coagulation; right, slow coagulation into water.

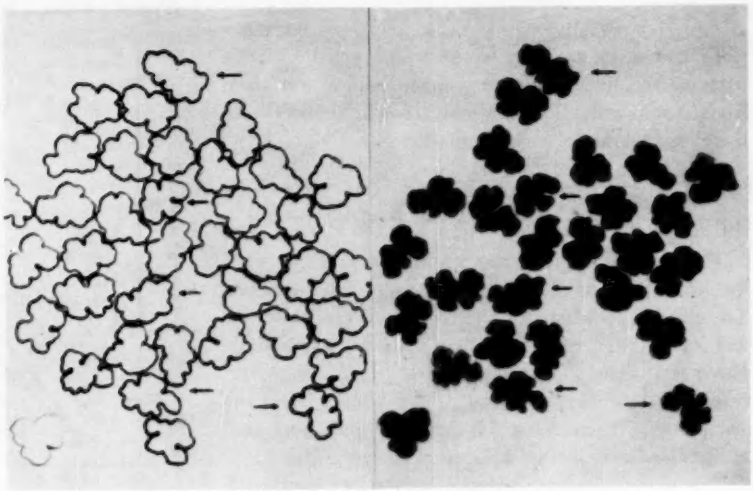


Fig. 3. Cross-sectional views of the same dry spun CTA fibers before and after removal of a surface saponified layer. Left: Dry spun CTA saponified for 3 min. Saponified layer retained. Fiber cross-sections stained with direct dyestuff to show saponified layer. Right: Same cross-sections as at left, but saponified layer has been removed with Cuen. Fiber cross-sections were then stained for better photographic contrast. (Some sections have been lost in processing.)

A homogeneous model fiber with mechanical properties similar to those of the dry spun fiber was desired. The slow removal of solvent by water, a non-solvent, seemed to give the desired system.[3] The process used, as described in the literature [2], involved the spinning of the same dope (CTA in 90/10 CH_2Cl_2/CH_3OH) used for dry spinning into a water bath. This system was not investigated extensively since, as the data will show, the particular conditions used accomplished the desired result of producing a radially homogeneous fiber.

Having prepared fibers under conditions favorable to a skin–core structure and a homogeneous structure, attention was focused on removing surface layers to study fiber properties as a function of radius.

Surface layers of the CTA fibers prepared by both methods of spinning were converted to cellulose by a heterogeneous saponification in 50 g./l. NaOH solution at 95° C. with a liquor to fiber ratio of 1000:1. The thickness of the saponified layer was controlled by the immersion time in the saponification bath.

Samples were wet out in cold water containing 0.1 g./l. Triton T, then immersed in the saponification bath at 95° C. for times ranging from 30 sec. to 3 min., quickly transferred to cold running water after the allotted time, rinsed for 5 min., soured in 1% acetic acid for 15 min., finally rinsed again in running water for 15 min., and air dried.

The left half of Figure 3 shows the saponified layer formed in the dry spun CTA. A direct dyestuff is used to stain the cellulosic layer while leaving the acetylated region colorless. The saponifying process has not altered the original shape of the fiber, and the saponified layer follows the original contours of the fiber.

The cellulosic layer formed by the saponification treatment was dissolved in 50/50 cupriethylene diamine (Cuen)/water at room temperature by immersing the fibers in the cellulose solvent for 3 min., then washing out the Cuen in cold running water for 15 min., souring in 1% acetic acid for 15 min., rinsing in cold running water for 15 min., and allowing to air dry.

The right half of Figure 3 shows cross-sectional views of the same dry spun CTA, depicted on the left after removal of the saponified layer. This removal is seen to affect general fiber outline very little. A slight rounding of the sharp crenulations of the dry spun fibers occurs, but the general fiber outline is preserved and no evidence of fiber swelling is noted.

So-called "controls" of the CTA fibers were prepared by treatment in water for 3 min. at 95° C., rinsing, souring, rinsing, drying, followed by treatment in 50/50 Cuen/water for 3 min., rinsing, souring, rinsing, and finally air drying. This wet processing of control fiber was used to relieve internal strains set up during the spinning operations. The procedure was necessary to insure that any property differences found after surface layer removal by a wet processing treatment were due to radial heterogeneity and not to stress relief.

Results

To assess the amounts of surface removed, calculations of the fiber radii were made before and after surface removal. The original fiber radius was estimated using the following equation

$$r_0(\text{cm.}) = \left(\frac{dpf}{3.14 \times 1.3 \times 9 \times 10^5} \right)^{\frac{1}{2}} \quad (1)$$

This equation gives the radius of a circle with the same area as that of the average fiber section. The result approximates the true fiber radius of the wet spun CTA very well since this fiber is round. However, with the crenulated dry spun fiber the result is somewhat artificial. The results obtained are 1.0×10^{-3} cm. for a 3.7-den. dry spun fiber and 1.56×10^{-3} cm. for an 8.9-den. wet spun fiber.

The equivalent radii of the variously desurfaced fibers were calculated by the following formula

$$r_x = r_0(1 - (w_0 - w_x)/w_0)^{\frac{1}{2}} \quad (2)$$

where: r_x = equivalent radius (cm.) of the desurfaced material after x min. in saponification bath followed by surface removal in Cuen; r_0 = equivalent radius (cm.) of original material; w_0 = weight (g.) of original material; and w_x = weight (g.) of desurfaced material. The estimate of the thickness of surface removed for any treated fiber is estimated by subtraction of the desurfaced radius from the original radius, that is,

$$r_0 - r_x \doteq \text{thickness of surface removed by treatment.} \quad (3)$$

The accuracy of this value for the round wet spun fiber appears adequate, but the values obtained in the case of the crenulated dry spun fibers are somewhat in doubt. However, because no major shape change occurs during surface removal, the values obtained by subtracting the estimated radii after varying amounts of desurfacing from the original radii are proportional to the true values of thickness of surface removed, and therefore do not affect the conclusions reached.

Over the limited range investigated and within the precision of the methods employed, the plot of equivalent thickness of surface removed as a function of saponification time yields a straight line for both dry and wet spun CTA (Figure 4), indicating that saponification rate does not change with the thickness of surface saponified. The weight loss

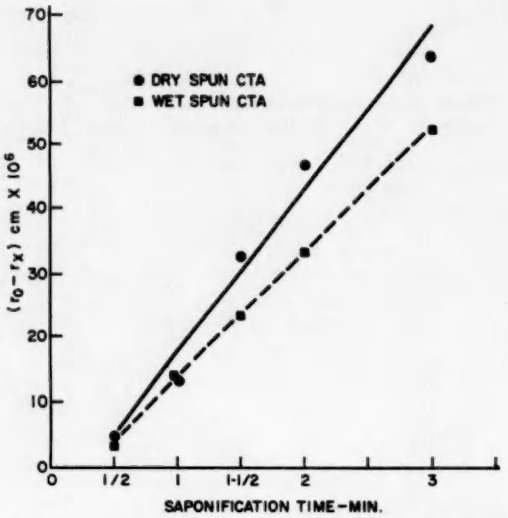


Fig. 4. Thickness of surface of fiber removed as a function of saponification time followed by treatment in 50/50 Cuen/water.

versus time relationship also results in a straight line plot, but this is not unexpected because the weight losses span a narrow range. Hence, the mechanism of saponification cannot be distinguished; that is, limitations in the accuracy of determining the exact amount of fiber removed prevent the distinction between a diffusion controlled reaction and a reaction governed by the rate of conversion of triacetate to cellulose.

There appears to be some difference in the rates of saponification of these dry and wet spun CTA's, with the dry spun fiber saponifying more rapidly. This may be due to the somewhat higher surface to volume ratio of the irregularly shaped dry spun fiber. (Both fibers have essentially smooth surfaces.)

Table I lists the total length shrinkage after saponification and after surface removal. The shrinkages occurring in processing of the controls are included for comparison. The data indicate that the total shrinkage occurs in the control wet treatment at 95° C. with no additional shrinkage occurring in the presence of alkali.

Acetyl values (percent acetic acid) were determined on the CTA samples before and after surface removal; these data are compared in Table II. The retention of the original level of acetyl values after fiber desurfacing indicates the presence of a sharp boundary between the cellulose and triacetate layers,

TABLE I. Length Shrinkage Resulting from Desurfacing

Fiber	Total percent length shrinkage after: Saponification	Total percent length shrinkage after: Surface removal	Percent length shrinkage resulting from control treatment
Dry spun CTA	1.9	1.9	1.9
Wet spun CTA	1.0	1.0	1.0

TABLE II. Acetyl Values of Control and Desurfaced Fibers

Fiber	No treatment	Control (3 min. Cuen treatment)	After desurfacing
Dry spun CTA	61.1	61.1	61.4
Wet spun CTA	61.6	61.6	61.6

with the cellulosic layer being completely removable by treatment in 50/50 Cuen/water. However, slight staining occurred when the desurfaced samples were dyed with a direct dyestuff. It is logical that a triacetate molecule at the interface of the cellulose and triacetate layers may be only partially saponified while still being held to the triacetate matrix by the unsaponified portion. The presence of hydroxyl groups on the surface of the desurfaced fibers is immaterial to this investigation as they would be present in both the dry and wet spun fibers. These two materials behave quite differently, as will subsequently be shown, in respect to the effect of surface removal both on physical properties and on rate of dyeing.

Treatment of the controls in the 50/50 Cuen/water solution does not affect the fiber acetyl value.

X-ray diffraction patterns and birefringence measurements were made on samples before and after surface removal. No changes could be found.

All these measurements indicate that the surface saponification and subsequent removal leaves a residual fiber with structure identical to that occurring in its equivalent volume in the original fiber.

With an Instron tester, tensile tests were made on the fibers before and after surface removal. A 60% per min. strain rate and a 10-in. gauge length were used. Figure 5 shows tenacity and elongation plotted against equivalent thickness of surface layer removed $(r_0 - r_x)$ for the triacetate fibers tested. In the case of the dry spun CTA fiber, elongation

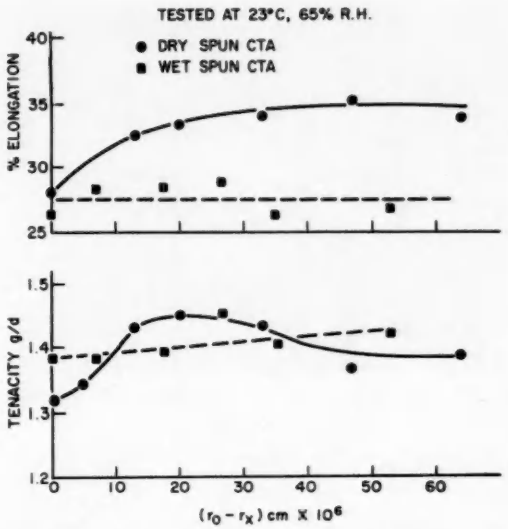


Fig. 5. Effect of surface removal on fiber tensile properties.

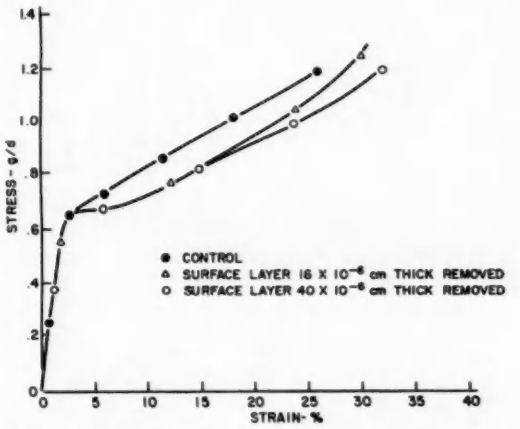


Fig. 6. Stress–strain curves of dry spun CTA before and after surface removal.

increases with increasing thickness of surface removed, up to a limiting value. In the case of the wet spun fiber, the elongation is independent of the amount of surface removed.

The tenacity of dry spun fiber exhibits a maximum when 15–20 × 10^{-6} cm. of surface has been removed, the surface removal necessary for maximum tenacity being less than that required to attain constant elongation. The tenacity of wet spun fiber is unchanged by surface removal.

The effect of desurfacing on the stress–strain behavior of the dry spun CTA is shown in Figure 6.

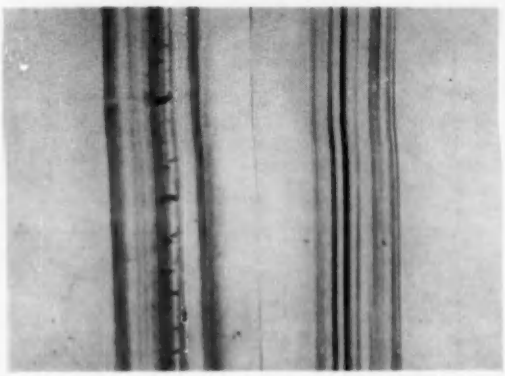


Fig. 7. Surface views of dry spun fiber after stretching. Left, control fiber; Right, desurfaced fiber.

There appears to be little change in the modulus and yield point with desurfacing. However, post-yield behavior is altered considerably. The lower stress level for a given elongation just above yield followed by a work hardening effect (increase in the rate of stress development for a given increment of strain) is typical of the behavior of a flexible structure capable of being oriented prior to break. The control fiber does not show this work hardening; the changing tensile behavior with varying degree of surface removal is indirect evidence that a less extensible component (a skin) is present in the original dry spun triacetate fiber, which prevents the fiber from attaining its maximum ultimate strength and elongation during tensile straining. Photomicrographic observations of the dry spun CTA fiber strained to break in tension have shown the formation of lateral cracks well before rupture. Figure 7, control and desurfaced dry spun fibers strained to 20% extension, shows lateral surface fissures in the control and none in the desurfaced fiber. These observations indicate a less extensible surface structure in the control than in the desurfaced material; this would bear out the hypothesis that orientation gradients exist in this model dry spun fiber. Surface failures may cause premature fiber rupture through crack propagation, thus reducing ultimate rupture strain and breaking stress.

In an attempt to determine more directly the nature of the skin structure, birefringence measurements were made on the dry spun fiber with successively greater degrees of surface removal. The Becké line technique, which is largely a measure of surface refraction, was utilized. Unfortunately, due to the inherently low birefringence of cellulose triacetate, no differences could be detected. Also, examination of saponified layers *before* removal in Cuen did not show a sufficient degree of birefringence for measurement, primarily due to the thinness of the saponified layer. Accordingly, no direct measurements of the structure of the skin could be obtained. However, the low extensibility of the skin on the dry spun fiber, together with the lack of crystallinity, suggests an increased degree of molecular orientation near the fiber surface.

The slight reduction in tenacity of the dry spun CTA after the removal of a surface layer 20×10^{-6} cm. thick may indicate defective fiber structure or

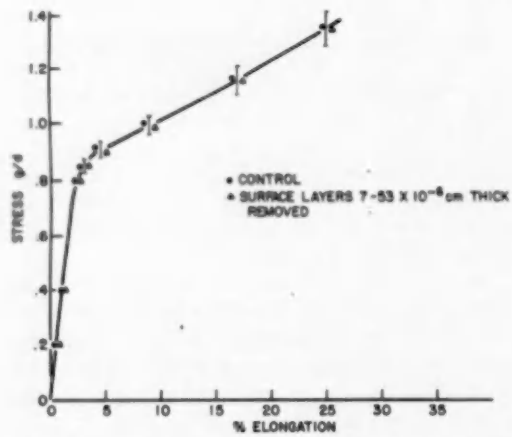


Fig. 8. Stress–strain curves of wet spun CTA before and after surface removal.

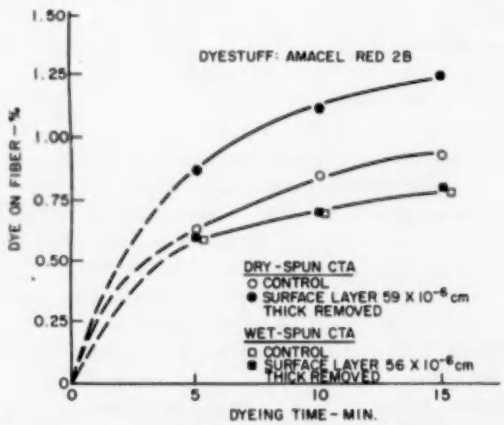

DYE ON FIBER - %
DYEING TIME - MIN.
DYESTUFF: AMACEL RED 2B
DRY-SPUN CTA
○ CONTROL
● SURFACE LAYER 59 X 10⁻⁶cm THICK REMOVED
WET-SPUN CTA
□ CONTROL
■ SURFACE LAYER 56 X 10⁻⁶cm THICK REMOVED

Fig. 9. Effect of surface removal on dye uptake as a function of time. Dry and wet spun CTA.

the creation of flaws, or it may merely reflect the lower orientation or "cheesy" structure of the core material.

Figure 8 indicates the unchanged stress–strain behavior upon removal of the surface of the wet spun CTA fiber. These data, together with the unchanging tenacity and elongation with varying amounts of surface removal, suggest radial homogeneity of the wet spun CTA throughout the thickness of surface removed.

The skin–core structure in the dry spun CTA fiber would be expected to affect dyeability in much the same way as has been shown in the case of viscose rayon. To illustrate this point, samples of the dry and wet spun fibers, before and after desurfacing, were dyed in a 5 g./l. dispersion of Amacel Red 2B at 95° C. for times of 5, 10, and 15 min. The dyebath contained 1 g./l. Igepon T-51 and 1 g./l. Calgon. The liquor to fiber weight ratio was about 800:1. These conditions were selected to approximate infinite dyebath conditions and to give indications of initial dyeing rates. The dye uptake as a function of time is shown in Figure 9.

The dyeing behavior of the wet spun CTA is substantially unaltered by surface removal while that of the dry spun CTA is significantly changed. For the dry spun material, the data indicate an increase in the initial dyeing rate (with Amacel Red 2B) due to surface removal. This is evidenced by a displacement of the rate curve; hence, the removal of surface material from dry spun CTA fibers appears to increase the rate of dye diffusion. This is seen in Figure 10 where the desurfaced fibers show a thicker as well as a more intense ring dyeing.

The data in Figure 11 illustrate the improved dyeing rate of the dry spun CTA with various amounts of surface removal. The improvement in dyeing rate due to surface removal in excess of 59×10^{-6} cm. is small.

The possibility that the improved dyeing rate was caused solely by an increased surface to volume ratio was eliminated as follows. Calculations of fiber surface to volume ratios were made (using "equivalent" radii) before and after various extents of desurfacing. The data were computed as percent change in surface to volume ratio due to desurfacing, by the following equation

$$S/V \text{ ratio} = 2\pi rl/\pi r^2 l = 2/r$$
$$\% \text{ change in } S/V \text{ ratio} = 100[(r_o/r_x) - 1] \quad (4)$$

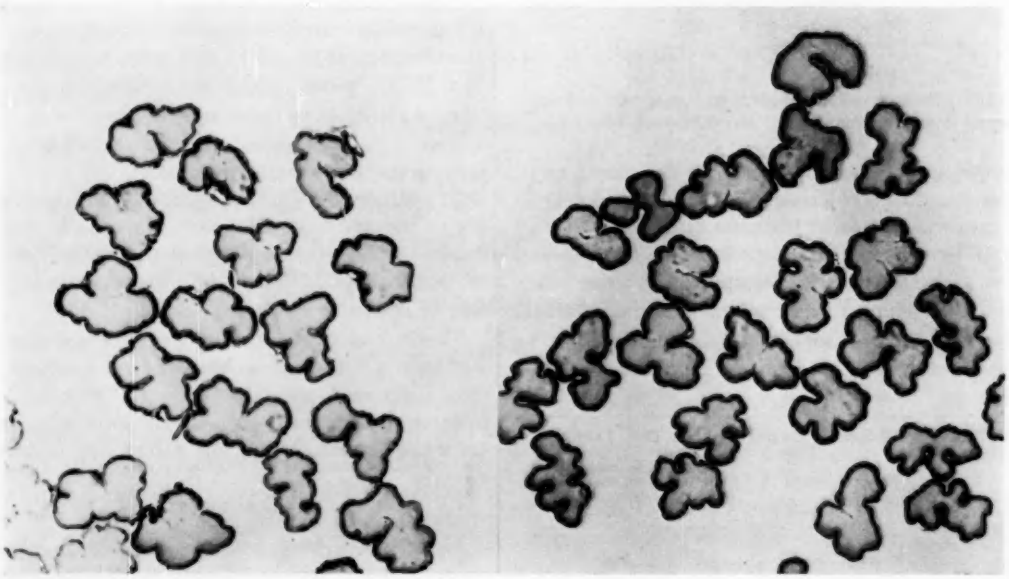


Fig. 10. Cross-sectional views of dyed dry spun CTA before and after surface saponification and removal. Left: Dry spun CTA control. No surface saponification. Cuen treatment as control. Dyed 15 min. in infinite dye bath of Amacel Red 2B. Right: Dry spun CTA. Surface saponification for 2 min. Cellulosic layer dissolved and fiber then dyed 15 min. in infinite dye bath of Amacel Red 2B.

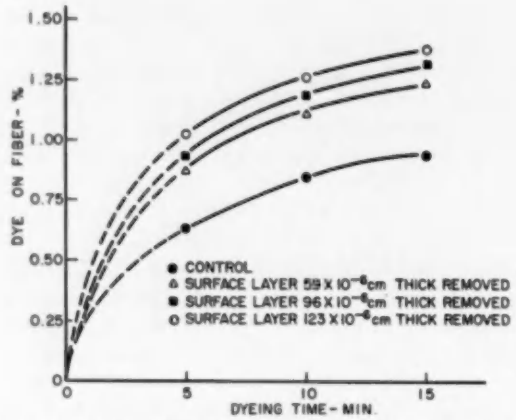

DYE ON FIBER - %
DYEING TIME - MIN.
● CONTROL
△ SURFACE LAYER 59 X 10⁻⁶cm THICK REMOVED
■ SURFACE LAYER 96 X 10⁻⁶cm THICK REMOVED
○ SURFACE LAYER 123 X 10⁻⁶cm THICK REMOVED

Fig. 11. Effect of varying amounts of surface removal on dye uptake as a function of time; dry spun CTA.

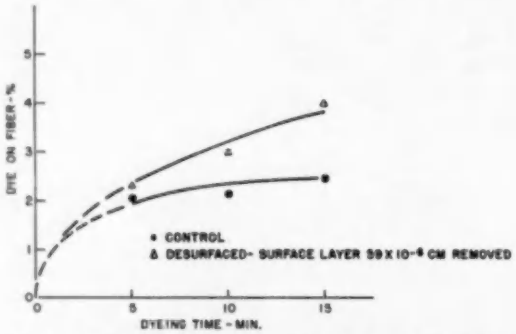


Fig. 12. Effect of surface removal on dye uptake as a function of time; dry spun CTA. Dyestuff—I.C. Blue GSF.

where r_0 and r_x are the original and desurfaced radii, respectively. The incremental improvement in dyeing rate was calculated from the data shown in Figure 11 by averaging the data over the three dyeing times. These values are compared with the incremental change in surface to volume ratio in Table III.

At the level of surface treatment resulting in removal of 59×10^{-6} cm., the increased dye rate

TABLE III. Effect of Desurfacing on Dye Take-up

	S/V increase, %	Increase in dye take-up,* %
Effect of reduction of radius of control by 59×10^{-6} cm.	6.0	34.6
Effect of further desurfacing from 59×10^{-6} cm. to 96×10^{-6} cm.	4.7	6.2
Effect of further desurfacing from 96×10^{-6} cm. to 123×10^{-6} cm.	2.7	3.8

* Average over 3 dyeing times (5, 10, and 15 min.) Amacel Red 2B dyeing.

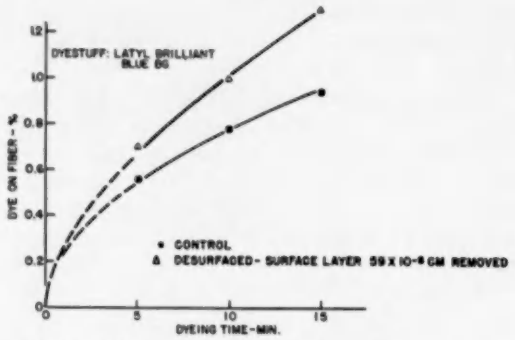


Fig. 13. Effect of surface removal on dye uptake as a function of time; dry spun CTA.

is far greater than the increased surface to volume ratio, suggesting that the effect is due mainly to the varying fiber structure near the surface. The displacement of the rate curves with more extensive surface removal, however, is roughly proportional to the increase in surface to volume ratio. It is significant to note that the thickness of the layer influencing the dyeing rate is of the same order of magnitude as the thickness influencing fiber elongation. This suggests even more clearly the presence of a skin on the dry spun CTA.

Similar changes in dyeing rates of the dry spun CTA due to surface removal are evidenced with Interchemical Blue GSF and with Latyl Brilliant Blue BG (Figures 12 and 13). Here, the observed increases in rate are much more pronounced as demonstrated by the marked changes of slopes of the rate curves with surface removal.

In addition, the rate curve for a conventional dyeing of the dry spun CTA shows a considerable increase in rate of exhaustion of the dyebath due to surface removal (Figure 14) thus confirming the infinite dyebath rate data.

The lack of change in the dyeing behavior of the wet spun CTA after surface removal indicates the effects observed with the dry spun CTA to be a function of fiber structure rather than of any chemical change resulting from the desurfacing treatment.

Summary

Model fibers have been prepared from cellulose triacetate under widely differing rates of coagulation. Rapid coagulation was achieved by a dry spinning process where solvent was flashed rapidly from the fiber surface, while slow coagulation was achieved by

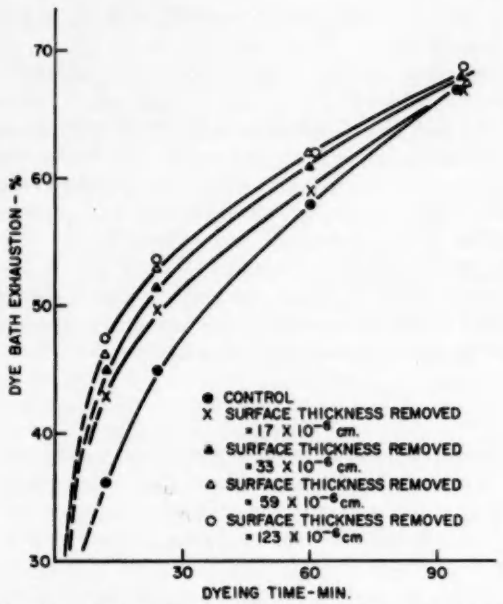


Fig. 14. Finite bath dyeing of desurfaced dry spun CTA. Dyestuff—1% Interchemical Blue GSF.

a wet spinning process wherein the solvent was leached out with water.

Surface layers have been removed from the fibers by heterogeneous saponification and dissolution of the saponified material.

Mechanical and dyeing properties were improved by desurfacing the rapidly coagulated fiber, but remained unchanged for the slowly coagulated fiber, indicating skin formation to be associated with rapid coagulation. The presence of a less extensible skin on the rapidly coagulated fiber has been further demonstrated by the decrease in lateral crack formation dependent on axial strain upon surface removal. This, coupled with the lack of crystallinity, suggests that the radially dependent mechanical and dyeing properties are associated with an increasing degree of molecular orientation near the fiber surface.

Literature Cited

1. Celanese Corporation of America, U. S. Patent 2,805,490 (September 1957).
2. Celanese Corporation of America, British Patent 793,222 (April 1958).
3. Celanese Corporation of America, U. S. Patent 2,839,420 (June 1958).
4. Chamberlain, N. H. and Khera, M. P., *J. Textile Inst.* **43**, T123 (1952).
5. Goerner, Gustav W., U. S. Patent 3899 (July 1921).
6. Morehead, F. F. and Sisson, W. A., TEXTILE RESEARCH JOURNAL **15**, 443 (1945).
7. Peck, V. and Kaye, W., TEXTILE RESEARCH JOURNAL **24**, 295,300 (1954).
8. Scott, R. G. and Ferguson, A. W., TEXTILE RESEARCH JOURNAL **26**, 284 (1956).
9. Waters, E., *J. Soc. Dyers Colourists* **66**, 609 (1950).

Manuscript received March 27, 1961.

Theoretical Aspects of Hook Removal at Drafting Operations

V. B. Merchant

Khatau Mills Ltd., Byculla, Bombay 27, India

1. Introduction

Following the monumental work done by Prof. Morton and associates at the Manchester College of Technology on the different aspects of fiber arrangement in sliver, roving, and yarn, it is now widely realized that a drafting process leads to a reduction in the percentage of hooked fibers. It is of interest to find out whether this reduction of hooks (expressed as a percentage of total hooked fibers) is equal at the leading and the trailing ends or whether there is a preferential removal of hooks at either end. Clearly, if the latter is the case, it is possible to control the direction of feed in the drafting zone so that the majority of the hooks lie in the direction from which they are preferentially removed and so achieve a greater reduction in the number of hooks during the same drafting operations, than is otherwise possible.

Morton and Summers' [3] work suggests that during a drafting operation there is a preferential

reduction of leading hooks. Nield [4], also working with Prof. Morton, reported later, however, that the percentage reduction in both trailing and leading hooks is of the same order. Recent work done at "ATIRA" [1], on the other hand, clearly contradicts both the above findings and suggests that at a drafting operation, the percentage reduction in trailing hooks is much greater than that in the leading hooks. Working on CO2 cotton, it was found that the average trailer reduction during a passage of drawing is about 44% as against a leader reduction of only about 20%.

Since drafting is in essence a relative movement of some fibers in relation to others, one is tempted—following Newton's second law, that action and reaction are equal and opposite—to expect that the reduction in trailing and leading hooks must be of the same order, as has, in fact, been reported by Nield. A more thorough consideration of the process of drafting, as given in this paper, however, suggests that ATIRA's findings are in agreement with theoretical expectations and that a drafting process should, as reported by ATIRA, remove more of the trailing hooks than leading hooks.

2. Fiber Movement in a Drafting Zone

First of all let us reassure ourselves that there is nothing wrong with Newton's second law! If drafting were a relative movement of a given number of fibers in relation to an equal number of fibers, there is no doubt that both leading and trailing hooks would be reduced to the same extent by drafting. This is the case when a piece of sliver is pulled out as indicated in Figure 1. Under such conditions it may be rightly expected that the reduction in leading and trailing hooks, on pulling, will be of the same order.

However, during drafting there are always a greater number of fibers in the drafting zone moving at the back roller speed than at the front roller speed. That this is so, is easily realized if we consider the hypothetical case in which a strand of parallel fibers, all of equal length, is drafted between two pairs of rollers with a nip-to-nip setting equal to the fiber length (Figure 2).

If n_1 and n_2 represent, respectively, the number of fibers in the cross section of the material as fed and the number in the drafted material

$$n_2 = n_1/D \qquad (1)$$

where D is the draft between the two pairs of rollers.

Since all the fibers are parallel and of a length equal to the setting of the drafting zone, there will be no floating fibers in the drafting zone. A fiber between the nip of the back rollers will continue to move at the back roller speed until its leading end reaches the front roller nip (the trailing end being simultaneously released by the back roller nip) and would then continue to move at the front roller speed.

Since there are n_1 fibers in the nip of the back rollers, there will be n_1 fibers in the drafting zone moving at the back roller speed. And since there are n_2 fibers in the nip of the front rollers there will be n_2 fibers in the drafting zone moving at the front roller speed. Hence if D is the draft between the rollers, it follows from Equation 1 that the number of fibers in the drafting zone travelling at the back roller speed is D times the number of fibers travelling at the front roller speed.

Now, if L is the length of each fiber, the average

Fig. 1. Pulling a tuft of sliver.

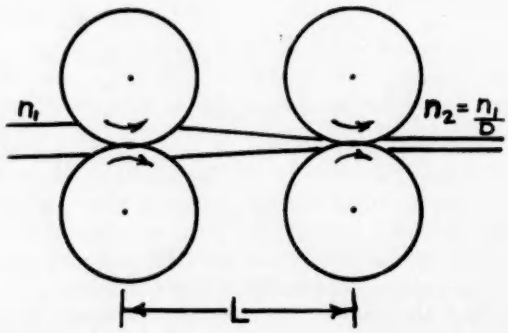


Fig. 2. Drafting a sliver between a pair of rollers set at a distance of staple length.

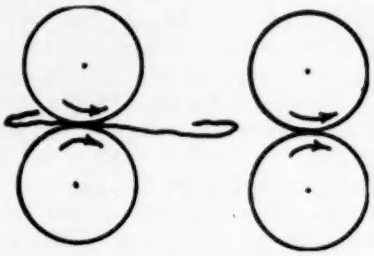


Fig. 3. Hooked fiber in a drafting zone.

length inside the drafting zone of both the fibers travelling at the back roller speed and those travelling at the front roller speed equals $L/2$. It follows therefore that the total surface area of fibers travelling at the back roller speed in the drafting zone is D times the surface area of fibers travelling at the front roller speed.

In practice, of course, the fibers may not all be of equal length; they can never all be straight and parallel, and the setting between the rollers is always slightly wider than the staple length of the fibers. Depending on the nature of the fiber-length distribution, degree of straightening and parallelization of fibers, and the roller setting, there will always be a certain percentage of floating fibers in the drafting zone, which may be expected to travel at a speed varying between that of the back and the front rollers. It is, however, reasonable to expect that in spite of this there will always be, in a drafting zone, a preponderence of fibers travelling at the back roller speed as compared to those travelling at the front roller speed; consequently the fiber surface area in a drafting zone travelling at the back roller speed is always in excess of that travelling at the front roller speed.

3. Forces Assisting and Resisting Hook Removal

Consider again a hypothetical case where all the fibers of equal length, having equal hooks at both the ends, and oriented parallel, are being drafted between two pairs of rollers set at a distance equal to the fiber extent. Figure 3 shows one such fiber in the drafting zone.

Removal of the Leading Hook

It will be clear from Figure 3 that in order to straighten out a leading hook the hooked length at the front of the fiber must travel at a faster speed than the rest of the fiber, which will be travelling at the back roller surface speed. The forces *resisting* this faster movement of the hooked portion of the fiber are: (a) the bending force required to straighten out the hook; (b) frictional force arising out of the surface contact of the hook portion of the fiber with fibers moving at the back roller speed. The force *assisting* the hook removal is: (c) frictional force arising out of the surface contact of the hooked portion of the fiber with fibers moving at the front roller speed.

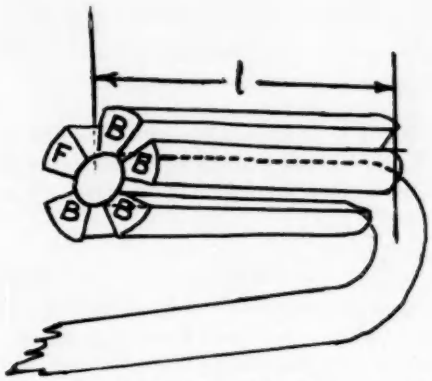


Fig. 4. A leading hook in frictional contact with surrounding fibers (B—fibers moving at back roller speed; F—fiber moving at front roller speed).

Evaluation of the Forces

Let

B = bending force resisting hook removal
D = draft between the two pairs of rollers
G = average lateral pressure exerted by one fiber on another
K = average ratio of the peripheral length of a fiber in contact with other fibers to the total peripheral length of fiber cross section
l = length of the hooked portion of a fiber
p = average peripheral length of fiber cross section
x = surface area in the hooked portion of the fiber in contact with fibers moving at the back roller surface speed expressed as a fraction of the total surface area in the hook region in contact with other fibers
μ = coefficient of interfiber friction.

Figure 4 is a simplified diagram showing fibers moving at back roller and front roller speeds bearing against the hooked portion (leading) of a fiber.

Considering the cross section of the hooked portion it is clear that

Total peripheral length in contact with other fibers $= Kp$

Hence,

Average area in contact with fibers moving at back roller speed (expressed as a fraction of the total area in contact with surrounding fibers) $= Kplx$ (2)

Therefore,

Average force opposing the movement of the hooked portion at a speed faster than the rest of the fiber (which is travelling at the back roller surface speed) $= \mu GKplx$ (3)

Now the fraction of fiber surface of the hooked portion in contact with fibers moving at front roller surface speed $= (1 - x)$. Hence,

Average force assisting the movement of the hook at a speed faster than the rest of the fiber $= \mu GKpl(1 - x)$ (4)

It has been shown in Section 2 that when a band of straight parallel fibers is drafted between a pair of rollers, set at a distance equal to the fiber length, the total surface area of fibers travelling at the back roller speed in the drafting zone is D times the surface area of fibers travelling at the front roller speed. It is easy to see that the same relation holds good with hooked fibers if the roller setting is made equal to the fiber extent rather than the fiber length.

Hence,

$$x/(1 - x) = D \tag{5}$$

Hence,

Resultant force assisting the removal of a leading hook

$$= [\mu GKpl(1 - x)] - [\mu GKplx] - B$$

$$= \mu GKpl(1 - 2x) - B$$

$$= -[\mu GKpl(2x - 1) + B] \tag{6}$$

$$= -\{\mu GKpl[(D - 1)/(D + 1)] + B\} \tag{7}$$

The negative sign of Equation 7 indicates that in general the forces resisting the removal of a leading hook exceed those assisting its removal. This, however, is not always so, since the relation given by Equation 5, $x/(1 - x) = D$, is true only on an average. There may be instances where the hooked portion of the leading hook of a fiber has more of its surface in contact with the fibers moving at the front roller surface speed than with those moving at the back roller surface speed. In such a case $(1 - x)$ will be greater than x, so that $(2x - 1)$ will be negative. From Equation 6 it is clear that under these conditions the forces assisting the removal of a leading hook may exceed those resisting it, and hence during drafting a leading hook may also straighten out. However chances of this happening are clearly remote.

Removal of the Trailing Hook

Contrary to the manner of the removal of a leading hook, the trailing hook is removed if the hooked portion of the fiber moves at a speed slower than the front roller surface speed when the rest of the fiber is moving at the front roller surface speed.

In this case the forces *resisting* hook removal are: (a) bending force required to straighten out the hook; (b) frictional force arising out of surface contact of the hooked portion of the fiber with fibers moving at the front roller surface speed. Clearly this force is equal to the force assisting the removal of the leading hook, i.e., $\mu GKpl(1 - x)$. On the other hand the force *assisting* the removal of a trailing hook is: (c) frictional force arising out of surface contact with fibers moving at the back roller surface speed when the rest of the fiber is moving at the front roller surface speed. This is clearly equal to the force resisting the removal of the leading hook, or $\mu GKplx$.

Hence,

Resultant force assisting the removal of a trailing hook

$$= [\mu GKplx] - [\mu GKpl(1 - x)] - B$$

$$= \mu GKpl(2x - 1) - B \tag{8}$$

$$= \mu GKpl[(D - 1)/(D + 1)] - B \tag{9}$$

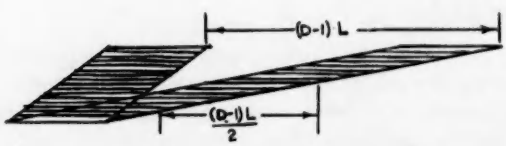


Fig. 5. Fiber movement during drafting.

Since D is always greater than 1 and B may be expected to be negligible in comparison to the frictional forces, the resultant force assisting the removal of a trailing hook is generally positive. Hence the trailing hooks are more easily straightened out.

4. Degree of Hook Removal

From Equations 7 and 9 it is clear that as the draft D increases the forces favoring the removal of a leading hook diminish and those favoring the removal of a trailing hook increase. If the draft is sufficiently high, none of the leading hooks will be removed and almost all the trailing hooks will be straightened out. On the other hand as D diminishes the chances for the removal of a leading hook increase and those for the removal of a trailing hook diminish, although, of course, the former will always be greater than the latter.

However at lower drafts it may happen that, although the frictional forces favor the removal of a hook, it may not be completely removed. This is because as the draft is reduced the average relative movement between fibers in a cross section also diminishes.

Arranging the fibers in the cross section of the material to be drafted *en echelon* as shown in Figure 5, it is clear that drafting causes an average relative movement equal to $(D-1)L/2$ between two fibers in a cross section of the undrafted material. If the hook extent of a fiber is greater than $(D-1)L/2$ it is unlikely that it will be removed completely during drafting, although it will undoubtedly be reduced.

5. Conclusions from the Theory

From the above theoretical discussion it is clear that a drafting process must preferentially remove trailing hooks. As the draft in a drafting zone is increased the chances for the removal of trailing hooks may be expected to increase and those for the removal of leading hooks diminish.

It would appear that the removal of hooks would be facilitated by:

(a) Concentration of draft in one zone rather than distributing it over several zones. At low drafts the distribution of frictional forces is such that it neither aids the removal of trailing hooks nor those of leading hooks.

(b) Increasing the compactness of the material fed to the drafting zone. This would increase the lateral pressure G. Since the bending force B may be expected to remain constant, it will be seen from Equation 9 that increase in G increases the resultant force aiding the removal of trailing hooks.

(c) Reducing the roller setting. This tends to decrease the number of floating fibers in the drafting zone and thereby enhance the difference between the forces assisting the removal of trailing hooks and those resisting it. It would be interesting to find out if the experimental results bear out the above conjectures.

6. Some Practical Applications of the Theoretical Findings

Spinning of Carded Yarns

According to the theory, a drafting operation preferentially removes trailing hooks, rather than leading hooks, the degree of preference increasing with the amount of draft. If this is so, one may expect that by feeding a roving to the ring frame so that the majority of hooks are in the trailing direction most of the hooks will be removed in the subsequent drafting operations and the resultant yarn will be stronger and evener. That this is so is clear from some recent findings at ATIRA [1]. Spinning 30s yarn from CO2 cotton and using different sequences of preparatory machines it was found that when roving was fed to the ring frame with the majority of hooks in the trailing direction: (a) yarn lea-strength was 11.8% higher and (b) Uster CV% of yarn was lower by 2.4 than when the roving was fed with the majority of hooks in the leading direction.

Since a card sliver has a far greater number of hooks in the trailing direction than in leading direction and since subsequent drafting at the draw frames and the speed frames is not expected to remove all the hooks, it follows that for efficient spinning there should be an odd number of machines between the card and the ring frame. Alternatively there may be an even number of machines between the card and the ring frame with one reversal of feed in between. This is supported by the findings of Tabata [5] et al.:

> To inquire into the bearing which the direction in which slivers are fed has on the quality of finished yarn, we have tried various directions of sliver-feeding and spun cotton yarns by the conventional Japanese system, i.e., passage of sliver successively through three drawing frames, a simplex frame and a ring spinning frame.

The results of this experiment show that the direction in which card sliver are fed to the subsequent process has some bearing on the quality of finished yarn, in that the lea strength of the yarn increases slightly when card slivers are fed to the drawing frame in the plus direction. (Normally, card slivers are fed to the drawing frame in the minus direction.)

Preparation of Comber Laps

The waste extracted at the comber for a given setting between the nippers and the detaching rollers depends on the orientation of the fibers in the combed fleece presented to the detaching rollers. Since the operation of combing by the cylinder will straighten out most of the leading hooks in the fleece, it is mainly the trailing hooks in the lap that matter. A reduction in these would lead to a reduction in waste without any deterioration in yarn quality. This fact is by now widely recognized, and it is for this reason that an even number of preparatory machines are kept between the card and the comber. In this way the trailing hooks which are in majority at the card become leading hooks in the comber lap as it is fed to the comber and are therefore more or less harmless.

A good lap preparation system should therefore primarily aim at reducing the number of trailing hooks in the comber lap. Since the fiber orientation at the comber is directionally similar to that at every alternate preceding machine, trailing hooks at the comber will be trailing hooks at these machines. Since drafting preferentially removes trailing hooks it follows that draft at these machines is more important than draft at other preparatory machines in the sequence. From this it follows that one-draw-frame lap-former (D-LW) system of lap preparation would be preferable to a sliver-lap ribbon-lap (SL-RL) system, since it is the draft in the first machine that is important and this is higher for a draw frame than for a sliver-lap machine. This is in agreement with the results obtained by Bogdan et al. [2], which are reproduced in Figure 6.

The present theory can also be used to explain the otherwise perplexing results obtained by Bogdan with a lap-winder drawing lap-winder (LW-D-LW) system of preparation also reproduced in Figure 6.

It was found that the waste obtained with the LW-D-LW system was almost 2% less than the waste obtained with a XLW-D-LW system.[1] Earlier in the present discussion it was pointed out that it would be preferable to have an even number of preparatory machines between the card and the comber since this would bring the majority of hooks in the comber lap in the leading direction, from which they can be more easily removed. The same effect can be secured in a three-machine preparatory system if a reversal is introduced at some stage in between.

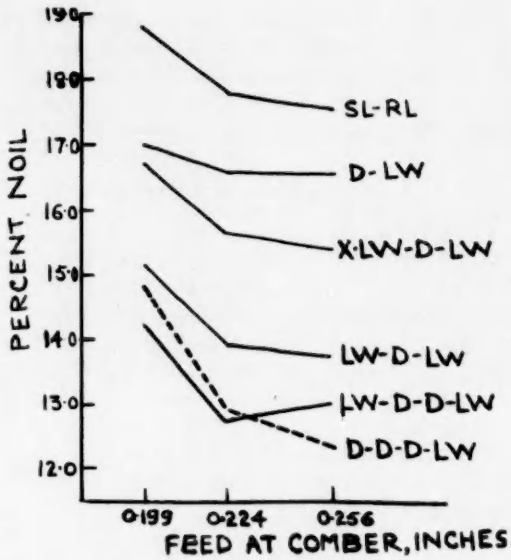


Fig. 6. Percent noil by lap preparation and feed (SL—sliver lapper; D—drawing; LW—lap winder; XLW—slivers reversed before lap winding).

Following this reasoning, one may expect a XLW-D-LW system of lap preparation to give less waste than a LW-D-LW system, whereas in fact the reverse is the case. This can be explained by the fact that the high draft at the lap drawing frame straightens out all the trailing hooks which are ultimately to lie in the trailing direction in the comber lap. In fact from the results it would appear as if the efficacy of the lap drawing frame in straightening out trailing hooks exceeds that of the comber cylinder in straightening out the leading hooks. This is not very surprising in view of the high draft at the lap drawing frame.

[1] LW-D-LW system with reversal of card sliver fed to the first lap winder.

Acknowledgment

The author wishes to thank the management of Khatau Mills Ltd. for their kind permission to publish this paper.

Literature Cited

1. Bahaduri, S. N., Garde, A. R., and Wakankar, V. A. (Ahmedabad Textile Industry's Research Association), private communication. *Editor's Note:* See p. 931, this issue.
2. Bogdan, J. F., Woo, H. K. C., and Pan, C. H., TEXTILE RESEARCH JOURNAL **29**, 741 (1959).
3. Morton, W. E. and Summers, R. J., *J. Textile Inst.* **41**, T349 (1950).
4. Nield, R., *J. Textile Inst.* **44**, 479 (1953).
5. Tabata, M., Hayakawa, K., and Takizawa, T., *J. Textile Machinery Soc. Japan* **6**, 5 (1960).

Manuscript received February 21, 1961.

Some Studies on the Formation of Hooks in Carding

V. A. Wakankar, S. N. Bhaduri, B. R. Ramaswamy, and G. C. Ghosh

The Ahmedabad Textile Industry's Research Association (ATIRA), Ahmedabad-9, India

Abstract

Hook formation at fiber ends and fiber disorder in the card sliver have been studied by using a fluorescent-tracer-fiber technique and Lindsley's method for measuring combing ratio. The rate of throughput at the card and the cylinder and doffer loadings have been shown to affect the proportions of the different types of hooks in the sliver. Other factors, such as the type of wire on cylinder and doffer, the action of flats, and the doffer comb speed, have been seen to have no influence on hook formation. Within the range of speeds investigated, the speed ratio between doffer and cylinder has little influence on hook formation. On the basis of the results obtained and the different hypotheses of Morton, it is suggested that the trailing and leading hooks are both formed at the junction of cylinder and doffer, but by different mechanisms.

Introduction

Morton and Summers [2] first demonstrated, by using a tracer-fiber technique, that the majority of fibers in card slivers are hooked and that trailing hooks are more numerous than leading hooks. They suggested a probable mechanism of such formation of hooks at card, but no evidence seems to be available to substantiate these hypotheses.

In the present paper the configuration of fibers in the card sliver is studied under different processing conditions. This has been done to isolate the factors associated with carding which are responsible for hook formation. On the basis of the results obtained, a probable mechanism of hook formation is suggested.

A new tracer technique, different from Morton's, has been used in the present work. Fibers dyed with fluorescent dye are used as tracers, and they are examined and counted under ultraviolet light.

A simple method of measuring the orientation of fibers in sliver and roving was reported by Lindsley [1]. The two measures used by him were "combing ratio" and "orientation index." Lindsley had perhaps not observed that a card sliver gives two distinctly different values for each measure of orientation, one when the combing is done in the direction of delivery of the sliver and one when it is done in the opposite direction. This was reported by Ramaswamy [3] in a later paper. The difference in these measures is attributed to the difference in the number and extent of the trailing and leading hooks. Along with the tracer-fiber technique this method has been used extensively in the present work for the quick assessment of fiber disorder. The term "fiber disorder" is used to denote factors such as lack of orientation along the axis of the sliver, crimp, hooks, and loops in fibers.

Methods of Determining the Fiber Configuration and Sampling Procedure

Tracer-Fiber Technique

The tracer-fiber technique used by Morton and Summers is somewhat complicated and time consuming, though very accurate. The following technique for counting hooks was used throughout the present work.

A small quantity of cotton fibers is dyed with commercial Tinopal BVN and opened on a Shirley Analyser. These fibers are mixed with blow room laps of the same cotton, on a finisher scutcher lattice. The percentage of tracers introduced is 0.25 on the weight of cotton processed. The lap containing the tracers is then fed to a card. After running the card with the lap containing tracers for 1 hr., by which time cylinder and doffer loading have been more or less stabilized, when samples are collected on 9×6 in. black boards marked with a reference direction. The web is carefully covered with a glass plate. About ten web samples are collected from different portions across the width of the card. When these samples are examined under a 1000-watt ultraviolet lamp in a dark room, the tracers become clearly visible. It is easy to count directly and classify the tracers after removing the cover glass. Each black board contains about 80 tracers. At least 500 such tracers are examined in each case. This process of counting and classification can be done within half an hour. With a magnifying glass and an ink pen the fiber contours can be easily traced on the cover glass and finally transferred onto white paper for permanent record. It is also possible to map the contours of the tracers when the samples are exposed to ultraviolet light under a microscope equipped with a Camera-lucida attachment, a very low magnification of 8× being used. This technique of mapping is rather time consuming and in the work described here the tracers were simply counted by categories. Data on fiber and hook extents are therefore not available.

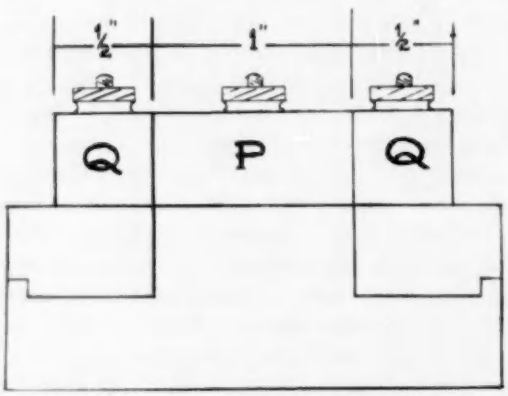


Fig. 1. Clamps for determination of combing ratio.

Measurement of Combing Ratio and Orientation Index

The technique and apparatus used by Lindsley have been somewhat refined to facilitate quick and easy determinations. A sliver is held securely under clamp P (1 in. width) and pair of clamps Q (½ in. width each) (Figure 1) and is trimmed with a razor blade close to clamps Q. The clamps Q are then removed and the fibers under them are gently combed several times along the axis of the sliver. During this process of combing, fibers that are not held by clamp P are combed out and collected (the weight of these is designated by C in the following equations); fibers extending from P but hooked, crimped, or lying at an angle to the axis of the sliver are straightened to their full length. This straightening makes some fibers extend beyond the clamps Q. Clamps Q are replaced and these extending ends (E) are trimmed by a razor blade. Clamps Q are once again removed and the fibers under them (N) are trimmed close to P. The three portions, of weights C, E, and N, for the left and right hand side are collected separately and weighed on a microbalance. The two measures of orientation that are obtained from the above quantities are

$$\text{Combing Ratio, CR} = C/(E + N) \quad (1)$$

$$\text{Orientation Index, OI} = [1 - (E/N)] \times 100 \quad (2)$$

It was observed during preliminary investigations that the estimates obtained of the orientation index had a wide margin of error since the weight E is only a few milligrams. In the subsequent studies, therefore, only the combing ratio was determined. In fact, for the measurement of CR only two quantities are necessary: the weight of the fibers that are combed out, C, and the weight of the fibers, H, remaining under the clamp P. The simplified expression thus becomes

$$\text{CR} = C/H \quad (3)$$

A few yards of the card sliver are collected as it comes out of the calender rollers, and the front end

of the sliver is twisted by hand to identify the direction. From this sample five small pieces of about 6 in. in length are randomly selected, each piece being also identified for direction. The five readings obtained from these pieces give a fairly accurate estimation of CR for a sample. Nevertheless, among these five sub-sample readings large differences are occasionally obtained. Normally (when the differences are not large) the range in the values of CR is about 0.15 for card sliver. The combing ratio in the forward direction (i.e., when the combing is done in the direction of sliver delivery at card) and the combing ratio in the backward direction (when the combing is done in the direction opposite to that of sliver delivery), hereinafter referred to as CR_F and CR_B, respectively, are estimated from the same piece of sliver, the distance between the two gripping points being only 1 in. (see Figure 1). Therefore, whenever one value of CR_F is higher than the other four the corresponding value of CR_B is also high, and thus the absolute difference in CR_F and CR_B values is very nearly constant for all five readings. One sample requires about an hour for cutting and weighing.

It was seen during a previous study that the CR_F and CR_B increase if the sliver is stored for a few days, probably on account of gradual disorientation and stress relaxations. Care was taken to maintain an equal interval between carding and testing for treatments between which comparisons were being made.

Effect of Hooks on Combing Ratio

Let us consider two slivers, identical in all respects except that in one all fibers are ideally straight and parallel, while in the other fibers are criss-cross, crimped, hooked, and looped. The CR for the first sliver can be calculated knowing the fiber-length distribution. Consider now the other sliver. A fiber in it becomes effectively shorter on account of hook, crimp, or loop formation or because it lies at an angle to the sliver axis. For such a fiber the chance of being gripped under clamp P is reduced while that of being combed out naturally increases. This sliver, therefore, will give a higher CR than the first.

The card sliver presents an interesting picture when visualized from the above point of view. It contains leading hooks, trailing hooks, and fibers hooked at both ends. The number of trailing hooks is about three times the number of leading hooks.

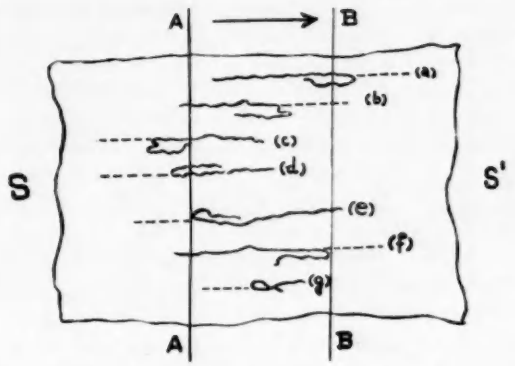


Fig. 2. Some typical hooks in card sliver.

Let SS′ be a card sliver (Figure 2). The arrow denotes the direction of delivery of the sliver at the card. Now consider some typical fibers in the zone AB. Fibers (a), (b), and (f) are hooked at their leading ends whereas the others are hooked at their trailing ends. The dotted line shows the original length of a fiber without hook. For simplicity of treatment fibers having hooks at both ends have not been considered.

Let the sliver be held at AA, trimmed at BB, and combed in the direction of the arrow for determining CR_F. The following table gives a qualitative estimate of the degree to which the various fibers, due to hook formation, will affect the quantities C and H of Equation 3.

It is thus evident that only the fibers of the type (e) substantially affect the combing ratio. The combing ratio increases due to such fibers. Though fibers (e) and (f) both have the same fiber and hook lengths, only fiber (e), which is a trailing hook, increases the value of CR_F, whereas the fiber (f) having a leading hook has only a moderate influence on CR_F. Similarly it will be seen that when the

TABLE I. Effects of Type of Fibers on Weights *C* and *H*

Type of fiber	*C*	*H*
a	Slight increase	No effect
b	No effect	Slight increase
c	No effect	No effect
d	No effect	Slight increase
e	Large increase	Large decrease
f	No effect	Slight increase
g	No effect	No effect

TABLE II. Estimates of Hooks and Fiber Disorder by the Two Methods

		Tracer technique					Combining ratio		
		Classification of fibers							
		Percentage occurrence							
Treatment	Doffer speed, r.p.m.	Hooks leading	Hooks trailing	Hooks at both ends	No hooks	Others	CR_F	CR_B	$(CR_F - CR_B)$
A	10.0	19	47	8	23	3	1.63	1.40	0.23
B	18.0	31	37	8	8	16	1.70	1.61	0.09

sliver is clamped at BB, trimmed at AA, and combed in the direction opposite to the arrow, in order to determine CR_B, fibers of the type (b) and (f), bearing leading hooks, increase the value of CR_B.

Since a card sliver, processed under normal working conditions, contains a greater proportion of trailing hooks than leading hooks, the value of CR_F is expected to be greater than CR_B. The larger extent of trailing hooks than that of leading hooks (as reported by Morton [2]) will further increase the difference between CR_F and CR_B.

From general considerations it is evident that the value of the combing ratio in a given sliver increases with (i) the width of clamp P, (ii) the fiber crimp, (iii) the lack of orientation along the sliver axis, (iv) the proportion of hooks, and (v) the extent of hooks. The difference in the values of CR_F and CR_B can only be due to the difference in the numbers of trailing and leading hooks and their extents, though the magnitude of this difference will depend on the clamp width. Values of the combing ratio in either direction are measures of fiber disorder. Equal values of CR_F and CR_B with a given clamp width may mean one of the following: (i) no hooks are present in sliver; (ii) the number of leading and trailing hooks and their extents are the same; or (iii) the number of trailing and leading hooks are different, but the combined effects of their number and extent are equal.

TABLE III. Length and Fineness Characteristics of Cottons Used

	Effective* length, in.	Mean* length, in.	C.V.,* % in length of fibers	Fineness,† μg./in.
CO2	1.10	0.90	32	4.2
Digvijay	1.00	0.84	27	4.1

* Determined from Baer Sorter patterns, by Clegg's construction.

† Determined gravimetrically.

Estimates of Hook Formation and Fiber Disorder by Tracer Techniques and Combing Ratio Measurements

As an illustration of the two techniques of measurement, consider the data shown in Table II. These refer to the Indian cotton CO2 processed at two different production rates.

There is a good correspondence between the two measures. Thus, in Treatment A the difference in the percentage of trailing and leading hooks is 28, while Treatment B gives a nominal difference of 6; correspondingly the difference between CR_F and CR_B is 0.23 for A and 0.09 for B. Further, as the number of fibers having no hooks decreases from 23 in A to 8 in B, the values of CR_F and CR_B also increase from 1.63 to 1.70 and from 1.40 to 1.61.

It is thus evident that with the measurements of CR_F and CR_B estimates of the fiber disorder and,

TABLE IV. Settings and Speeds at Card

Speed		Settings, 1/1000 in.	
Cylinder	170 r.p.m.	Cylinder to Licker-in	7–9
Licker-in	560 r.p.m.	Cylinder to Doffer	7
Doffer	Varying	Cylinder to Flats	10 (Uniform)
Flats	2 in./min.	Licker-in to Feed Plate	12
Doffer Comb	2350 strokes/min.	Doffer to Doffer Comb	12

in particular, of the difference in the number of hooks and their extents can be obtained indirectly.

The percentages of the various types of fiber as obtained here for an Indian cotton at normal doffer speed (Treatment A) are in close agreement with the data published by Morton for an Egyptian cotton and for Fibro. It also agrees with the data published by Wilhelm and Wagner [4] for Egyptian and Peruvian cottons. Thus it may be presumed that the pattern of hook formation is not affected by fiber properties, such as length and fineness, nor by the variety of cotton.

Experimental Conditions

Two Indian cottons, CO2 and Digvijay, of the fiber characteristics shown in Table III, were generally used in this study.

The investigations were carried out, unless otherwise stated, on a standard 40 in. width MMC revolving flat card. The card had normal flexible fillet. The settings and speeds shown in Table IV were employed.

Fiber Disorder in Card Sliver under Different Processing Conditions

Effect of Different Production Rates

It is generally known that quality in carding deteriorates at higher production rates. The fiber disorder at different rates of production was therefore studied first. The production rate was increased by increasing the doffer speed; four doffer speeds were used. The card was run at each speed for an hour after initial stripping, and samples for the determination of the combing ratio were collected at the end of this period. The results are given in Table V.

As the rate of production increases, the level of the combing ratio slowly increases, indicating that there is an increasing trend toward fiber disorder. The difference $CR_F - CR_B$ decreases with increasing production rate. Though the differences between the values of CR_F and CR_B for the first three production rates may not be statistically significant, yet they are indicative of the changing pattern of the hooks. This change appears to be very sudden at some production rate between 15.0 and 20.0 lb./hr. At the 20.0 lb./hr. production rate, CR_F and CR_B are almost equal, showing that the combined effects of the number and extents of trailing and leading hooks have become almost equal. From Table II, which also shows the effects of an increase in production rate, it appears that at a high production rate the number of leading hooks has increased considerably while that of trailing hooks has actually decreased.

It thus appears that increasing the production rate by increasing doffer speed affects the pattern of hook formation at card. During this process, however, the following factors have changed: (i) cylinder and doffer loading, (ii) ratio of the surface speeds of cylinder and doffer, (iii) the flat loading, and (iv) number of strokes of the doffer comb per inch of web delivered. It was not yet known which of these factors contributed most towards the formation of hooks. Subsequent experiments were planned so that only one factor was changed at a time.

Effect of Cylinder Loading: Extended Stripping Cycle

In an experiment with a production rate of about 10 lb./hr. the stripping cycle was extended to 12 hr. This kept the rate of throughput and the speed ratio of cylinder to doffer constant, but resulted in progressively more cylinder and doffer loading with time. The flat loading may have increased slightly.

Since this study was also combined with some other investigations, only a limited number of read-

TABLE V. Production Rate at Card and Fiber Disorder
Cotton: CO2

Doffer, r.p.m.	Production rate, lb./hr.	Combing ratio		$CR_F - CR_B$	Cylinder* load, g.	Doffer* load, g.
		CR_F	CR_B			
5	5	1.65	1.45	+0.20	59	6
10	10	1.77	1.60	+0.17	95	10
15	15	1.82	1.67	+0.15	103	13
20	20	1.93	1.95	−0.02	126	15

* Weight of stripping at the end of 1 hr.

TABLE VI. Stripping Interval—Fiber Disorder

Samples collected at the end of	Combing ratio			Cylinder load, g.	Doffer load, g.
	CR_F	CR_B	$CR_F - CR_B$		
2 hr.	1.73	1.44	+0.20	105	16
12 hr.	1.92	1.84	+0.08	265	41

TABLE VII. Hook Formation with Metallic Wires

Percentage occurrence

Hooks leading	Hooks trailing	Hooks at both ends	No hooks	Others
11	55	8	20	6

TABLE VIII. Production Rate and Fiber Disorder on Metallic Wire

Production rate, lb./hr.	Combing ratio		$CR_F - CR_B$
	CR_F	CR_B	
10.0	1.69	1.49	+0.20
20.0	1.95	1.92	+0.03

ings could be collected on cylinder and doffer loading and the combing ratio. The results are given in Table VI. A slightly different mixing (80% CO2 + 20% Vijay) was used in this experiment. But it has been pointed earlier that this is not likely to have any effect on the degree of hook formation.

These data show that with longer stripping intervals and greater loading on cylinder and doffer the difference $CR_F - CR_B$ decreases, indicating that the proportions and extent of trailing and leading hooks are nearing equality. The general fiber disorder also increases, as can be seen from the increasing values of the combing ratios.

Hook Formation on Metallic Wire Card

The formation of hooks on a card fitted with metallic wires on cylinder and doffer, in which no loading of these components takes place, was next examined. Since little information has been published on fiber arrangements with these types of wires, data were collected using the tracer-fiber technique. Digvijay cotton was carded on a standard 40 in. width Tweedale and Smalleys card equipped with J. W. & H. Platts' Metallic Card Clothing on cylinder and doffer and with flexible wires on flats. Other settings and speeds were more or less the same as for the MMC card except that flats were set at 7 in./1000 to the cylinder. Web samples were collected after a 45-min. run. A 7-lb./hr. production rate at a doffer speed of 7 r.p.m. was used here. The data are presented in Table VII. The proportions of the hooks of different categories obtained are very similar to those obtained with flexible fillet (see Table II, Treatment A). The majority of fibers are hooked either at one end or at both ends and there is a preponderance of trailing hooks.

Effect of Higher Production Rate on Metallic Wire Card

This investigation was made primarily to observe the type of fiber disorder at higher production rates when the cylinder and doffer loading is practically nil. Two production rates, 10.0 and 20.0 lb./hr., were obtained by employing 10.0 and 20.0 r.p.m. of doffer. The CO2 cotton was used for this study. Other settings and speeds were the same as in the above experiment. Samples of sliver were collected for determination of the combing ratio after an initial run of only 20 min. The results are shown in Table VIII. As with the flexible fillet card, a higher CR and lower difference between CR_F and CR_B are noticed at the higher production rate. This shows that a widely different type of cylinder and doffer clothing does not alter the pattern of hook formation.

Effect of Flats on Hook Formation

On the MMC card which was equipped with flexible wire fillet on the cylinder and doffer, the flats were removed and in their place a masonite cover was fixed, the polished surface facing the cylinder. The cover was securely fixed over the flexible bends so as to have minimum air leakage; separate linings were provided over the front and back plates. The distance between the cylinder wire points and the masonite cover was more than $\frac{1}{8}$ in. All other settings and speeds were the same as given earlier. Data on fiber arrangement were obtained for Digvijay cotton at a doffer speed of 10 r.p.m. corresponding to a production rate of 10 lb./hr.

(Table IX). There is hardly any difference in the two sets of figures. The flats do not appear to play any significant part in the formation of hooks.

Speed Ratio between Cylinder and Doffer

It was seen earlier that the rate of production affects the formation of hooks. The rate of production had been increased by speeding up the doffer, i.e., the speed ratio between cylinder and doffer had decreased with increasing production. Some attempts are made here to isolate these two aspects, viz., rate of production and the speed ratio between cylinder and doffer.

At each of the three doffer speeds of 8, 14, and 20 r.p.m., three rates of production were obtained by changing the pinion driving the feed roller. Sliver was thus available at three production rates for a given speed ratio of cylinder and doffer. Also production rates of 11, 20, and approximately 15 lb./hr. were obtained, each at two different speed ratios of cylinder and doffer. Other speeds and settings were as given earlier, but in place of flats a masonite cover was used. The samples were collected for each trial after an initial run of only 10 min., when the cylinder and doffer loadings were very much less than under normal working condition. The absence of flats would also contribute to a lower loading of cylinder. This study (see Table X) was undertaken with the Digvijay cotton.

At equal or nearly equal production rates, but at different ratios of cylinder to doffer speed, the percentages of leading and trailing hooks are as follows:

Production rate, lb./hr.	Sliver	Cylinder/doffer speed ratio	% Trailing* hooks	% Leading* hooks
11	C	40	62	20
	D	21	60	25
14–15	E	21	55	25
	G	16	54	27
20	F	21	59	25
	H	16	57	34

* Including fibers hooked at both ends.

It would thus appear that in the range of speed ratios used, the relative speed between doffer and cylinder has no effect on the formation of trailing hooks and very little, if any, on the formation of leading hooks.

The total percentage of trailing hooks fluctuates between narrow limits (54–62) up to a production of 20 lb./hr. and then decreases appreciably to 46 at 27 lb./hr. The total percentage of leading hooks increases from a low of 15 at 6 lb./hr. to between 20 to 24 at 8 to 20 lb./hr. and increases further to 41 at 27 lb./hr. (Figure 3). These results are qualitatively of the same type as those obtained earlier, except that significant changes in the proportion of trailing and leading hooks have occurred at a higher production rate than before. The higher level of production rate at which the effect is seen

TABLE IX. Effect of Flats on Hook Formation

	Percentage occurrence				
	Hooks leading	Hooks trailing	Hooks at both ends	No hooks	Others
Without flats	15	42	8	26	8
With flats	13	48	9	25	5

TABLE X. Hook Formation at Different Cylinder and Doffer Speed Ratios and Different Production Rates

Doffer, r.p.m.	Surface speed ratio between cylinder and doffer	Rate of production, lb./hr.	Sliver reference	Percentage occurrence of hooks				
				Hooks trailing	Hooks leading	Hooks at both ends	No hooks	Others
8	40	6	A	50	9	6	29	6
		8	B	50	12	9	23	6
		11	C	52	10	10	24	4
15	21	11	D	49	14	11	19	6
		15	E	46	16	9	22	7
		20	F	49	15	10	20	6
20	16	14	G	41	14	13	20	12
		20	H	41	18	16	18	11
		27	J	30	25	16	16	13

may be due to the lower loading of cylinder and doffer for a given production rate in this series of experiments compared to the trials mentioned earlier. Further, the difference between total numbers of trailing and leading hooks decreases with increase in production rate (Figure 4). This was noted in earlier experiment from values of $CR_F - CR_B$.

Attempts were made to obtain lower ratios of cylinder to doffer speed. With special arrangements the following conditions were tried. At the first

Production rate	Speed ratio cylinder/ doffer	Licker-in r.p.m.	Cylinder r.p.m.	Doffer r.p.m.
40 lb./hr.	1	120	25	46
	7.8	550	170	40

speed ratio only tufts were delivered discontinuously by the comb (which was run by a separate motor at 5500 strokes/min.) and no measurements on hooks could be made. At the higher ratio there was only a partial continuity in the delivery at the comb. It was difficult here to classify the shapes of the tracers, but well defined hooks were absent.

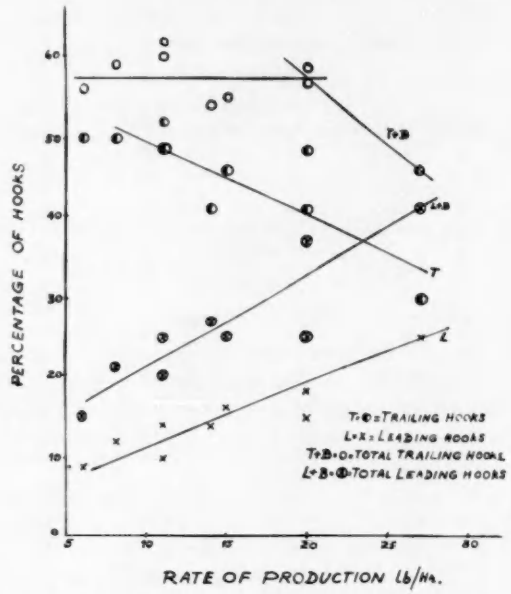


Fig. 3. Production rates at card versus number of hooks in card sliver.

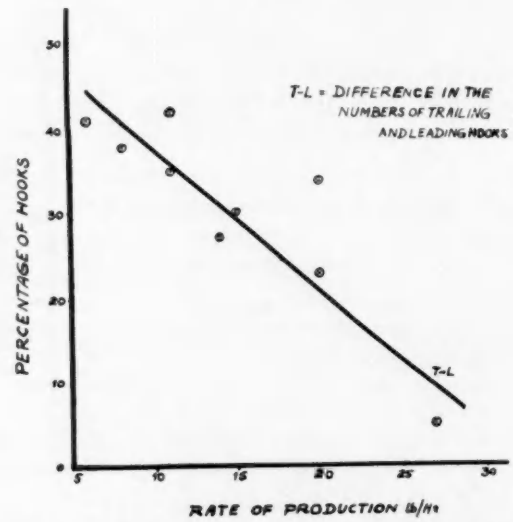


Fig. 4. Production rates at card versus difference in number of trailing and leading hooks.

Effect of Doffer-Comb Speed on Hook Formation

During the various experiments reported here, the doffer comb was vibrating at 2350 strokes/min. irrespective of doffer speed up to 20 r.p.m. The number of strokes of the comb per inch of doffer surface thus varied from 5.5 to 1.4 corresponding to 5 and 20 r.p.m. of doffer, or in other words, in one stroke of doffer comb 0.18 in. to 0.72 in. of web was peeled off by it. This aspect was investigated further by employing four comb speeds, 900, 1150, 1450, and 2350 strokes/min. at a doffer speed of 6.5 r.p.m. Data were obtained by employing the tracer technique as well as by estimating the combing ratio. No difference in the proportion of various types of hook was perceptible at the different speeds of the comb. Morton and Summers had suggested that the formation of leading hooks may be a consequence of doffer comb action. The results obtained here however, do not substantiate this view.

Discussion of Results

The experimental results obtained are discussed here in the light of the hypotheses put forward by Morton and Summers regarding the mechanism of hook formation.

Trailing Hooks

According to those authors, during the transfer of a fiber from cylinder to the doffer, the front end of the fiber gets lashed into the doffer and travels

with the speed of the doffer; the back end, which is still in contact with the cylinder (either directly or indirectly through an entanglement with other fibers on the cylinder), is travelling at the speed of the cylinder, which is greater than that of the doffer. The two ends are, thus, moving at different velocities; the front end, if firmly anchored in the doffer wires, will travel with the doffer and try to dislodge the fiber from the cylinder wire, but in the mean time the back end has rapidly moved downwards, thus forming a shape, similar to the head of a cane, termed a hook. These hooks will emerge as trailing hooks in the sliver.

Wilhelm and Wagner [4] have restated their faith in the above hypothesis without offering extra evidence for it. It follows from the hypothesis that at lower speed ratios of cylinder and doffer, the actual number of trailing hooks formed and/or their extents should be less. Unfortunately, data have been collected only on the occurrence of hooks and not on hook extents. The data on number of hooks show that up to the speed ratio of 16 there is hardly any decrease in the number of trailing hooks formed. It may be that a speed ratio of 16 is not sufficiently low to cause any significant difference in the formation of trailing hooks. It was found that at a speed ratio of 7.8, though it was extremely difficult to classify the fibers into different categories, no well defined trailing hooks could be isolated. While there may thus be some ground to believe that the formation of trailing hooks is reduced at lower cylinder to doffer surface speed ratios, further work is necessary to prove this point.

According to the hypothesis, trailing hooks are formed on fibers which are directly controlled by the doffer wire. If the thickness of fiber layer on the cylinder is sufficiently great, it is conceivable that only the fibers on the surface of the cylinder will have direct contact with the doffer wires while the lower layers will be peeled off by the doffer through contact with the top layer. Therefore, with increasing thickness of layer of fibers on the cylinder there should be a decrease in the proportion of trailing hooks. At a given cylinder speed, the density of fibers on the cylinder wire increases with rate of production. And it has been seen in both Tables II and X that the expected reduction in the total percentage of trailing hooks does take place at a sufficiently high rate of production.

In Table II the decrease in the number of trailing hooks is seen at 18 lb./hr. production while in Table X it is seen only at 27 lb./hr. It must be remembered that the cylinder loading for any given rate of production was much less in the latter than in the former set of experiments due to circumstances already mentioned. The rather sudden reduction in the proportion of trailing hooks (Table X) suggests that there is probably a threshold thickness of the layer on the cylinder wire beyond which only the formation of trailing hooks is affected.

Leading Hooks

In the opinion of Morton and Summers, the leading hooks are formed by one or more of the following three mechanisms:

1. During the transfer from cylinder to doffer a fiber, which is entangled with the doffer wires, gets its downward trailing end whipped up, due to relaxation, into the form of a hook immediately below the doffer setting point.
2. The hooks are formed by the action of doffer comb.
3. The fibers with leading hooks owe their origin to cylinder wires (though no satisfactory explanation has been given as to how these fibers were hooked around cylinder wires).

It is clear from the present data that the doffer comb speed does not exert any influence on the mechanism of formation of either leading or trailing hooks. The possibility that the leading hooks owe their origin to the cylinder wires themselves poses questions as to how these hooks are formed? Does this formation take place during the transfer of fibers from licker-in to cylinder or does it take place during the time when the fibers are sandwiched between cylinder and flats? The present data show that such hooks could not have been formed during the brushing action of cylinder and flats, since even after the removal of the flats, leading hooks are observed in the delivered web. No data are available to answer satisfactorily the first question, though independent investigations showed that the licker-in speed had no effect on the various types of hook.

The first hypothesis of Morton and Summers appears plausible from the data collected here. They suggested that the trailing end of a fiber, which is entangled with the doffer wire directly or indirectly, gets whipped up to form two tails of a hook immediately below the doffer setting point. The fibers

on the cylinder are in the form of a layer. The fibers which are on the surface of this layer are positively controlled by the doffer, their front ends form trailing hooks, whereas the lower layer is peeled off by the doffer only through its contact with the top layer. In this process of peeling off, the trailing ends which are embedded in the cylinder wires, after losing contact with the cylinder, get whipped up, due to sudden relaxation, and form hooks. These hooks will emerge as leading hooks in the web. It is understandable that with the formation of a thicker layer the proportion of fibers that are indirectly controlled increases and therefore the possibility of formation of leading hooks is also expected to increase.

The tendency noticed in our experiments (Tables II, V, VI, VIII, X) for the difference between the proportions and extents of leading and trailing hooks to be reduced or even eliminated completely at high loadings of cylinder or at high production rates can thus be satisfactorily explained. If the hook formation does take place in the above manner, it is apparent that a thicker layer will be formed at a comparatively lower production rate on a card fitted with metallic wires than on a card having a flexible fillet. It also follows that with metallic wires, the condition where an equal or nearly equal proportion of leading and trailing hooks is found can occur at a much lower production rate than with a flexible fillet.

Conclusions

1. The fiber disorder in the sliver increases with rate of production or loading of cylinder.

2. The number of leading hooks in the sliver increases with rate of production or cylinder loading; the number of trailing hooks shows a decrease at a sufficiently high rate of production or loading. At a very high rate of production, the number of leading hooks is nearly equal to that of trailing hooks.

3. The speed of doffer comb, the presence or absence of flats, or the type of wire used on cylinder and doffer (flexible or metallic) have no effect on hook formation.

4. The degree of hook formation is unaffected in the range of surface speeds of cylinder or doffer normally employed.

It is suggested that trailing hooks are formed at the junction of doffer and cylinder on fibers which are directly held by the doffer wires, the hook being imparted by the difference in surface speeds of doffer and cylinder. The leading hooks are formed on fibers which are peeled off by the doffer from the cylinder not directly but through contact with other fibers. The hook is imparted by the whipping up of the fiber due to relaxation below the doffer setting point.

Acknowledgments

We thank the Director and the Council of Administration of ATIRA for permitting us to publish this work. We are also grateful to Mr. P. K. Rao and Mr. A. R. Garde for helping us in preparing the present paper.

Literature Cited

1. Lindsley, C. H., TEXTILE RESEARCH JOURNAL **21**, 39 (1951).
2. Morton, W. E. and Summers, R. J., *J. Textile Inst.* **40**, P106 (1949).
3. Ramaswamy, B. R., *Proceedings of ATIRA Tech. Conf.* **B19** (1959).
4. Wilhelm, A. and Wagner, H., *Textil-Praxis* **12**, 223 (1957).

Appendix

We are aware of the objections to the use of dyed fibers as tracers. The dyeing may affect the frictional and other properties of the fibers. In order to verify that the use of fluorescent dyed fibers does not materially affect the configuration of fibers in the sliver the following investigation was conducted.

A 2-lb. lot of short staple Indian cotton was divided into two parts. One part was carded after preliminary opening on the Shirley Analyser (with wide settings between feed and licker-in). The other part was dyed with Tinopal BVN and after drying was opened in the Shirley Analyser and was then carded. The MMC card employed in our study was used in this investigation. Settings, production rates, and hank sliver were identical for the two samples. The combing ratios of the two card slivers were determined and are given below:

Combing ratios

Sliver	Forward	Backward	Difference
Undyed	2.07	1.56	0.51
Dyed	2.11	1.57	0.54

There is hardly any difference in the combing ratios and hence presumably in fiber disorder between the two samples. It was therefore concluded that the use of dyed tracer fibers would be justifiable for studying the configuration of fibers in card sliver.

Manuscript received April 20, 1961.

The Use of Coreactant Curing Agents with a Diepoxide to Impart Wrinkle Resistance to Cotton Fabrics

Robert M. Reinhardt, Russell M. H. Kullman, Harry B. Moore, and J. David Reid

Southern Regional Research Laboratory,[1] New Orleans, Louisiana

Abstract

Wrinkle resistance can be imparted to cotton fabrics with a diepoxide when certain coreactant curing agents are used. Such materials coreact to become a part of the finished product and introduce linkages and chemical groups which differ from those obtained when a true catalyst is used. Several coreactants including, for example, phthalic anhydride, citric acid, 1-aminoethyl-2-methyl-imidazoline, triethanolamine, and potassium thiocyanate, were used with 1,3-diglycidylglycerol as the diepoxide. In some cases mere deposition seemed to occur while in other cases cross-linkage was accomplished. Some indications of the types of reaction were obtained from infrared data and from the responses of the treated fabrics to various classes of dyes. In some cases coreaction between the diepoxide and the curing agent appeared to take place at relatively low temperatures, producing improved wrinkle resistance. Phthalic anhydride was used to investigate this aspect in more detail.

For comparison with the coreactant materials, several acid salts were used as catalysts, and the results are reported. Among the more suitable acid catalysts are magnesium perchlorate, aluminum sulfate, and zinc fluoborate.

The inorganic acid catalysts produced fabrics with excellent durability and wrinkle resistance. Tearing strength losses, however, were greater with epoxide-treated cotton than those observed, at equivalent crease recovery angle, when a typical methylolamide finishing agent with catalyst was used. The durability to alkaline solutions of some of the epoxide finishes applied with coreactant curing agents was not as good as that of fabrics prepared with the inorganic acid catalysts. Tearing strength and wrinkle resistance of epoxide-treated cotton can be improved by inclusion of additives such as polyethylene, acrylic polymer, or silicone, in the finishing bath.

Introduction

The search for new and improved wrinkle resistance finishes for cotton has resulted in a number of interesting, potentially valuable finishing agents. Among the non-nitrogenous types, the diepoxides have attracted much attention because of their resistance to laundering, particularly to damage by chlorine bleaching [5, 13]. Epoxides are now available commercially and have been used to some extent in cotton processing. In addition, the use of these compounds with methylolated nitrogenous agents in mixed or blended finishes has been reported [3]. In these mixed finishes, the proper combination of agents produces a finish with the more desirable characteristics of each of the components, particularly the increased resistance to chlorine damage. At this laboratory, both pure [2, 7, 8, 9] and blended finishes have been studied.

A deterrent to more widespread use of epoxides, in addition to price, is the general use of zinc fluoborate as a catalyst. The acidity developed by zinc fluoborate makes it a very efficient catalyst, but it also lowers fabric strength, and volatile fluorides are released during curing.

In the plastics industry, use of a number of coreactant "catalysts" or curing agents such as organic acids and anhydrides and substituted amines has been reported [6]. These materials become a part of the finished product and introduce linkages and chemical groups which are not obtained when a true catalyst

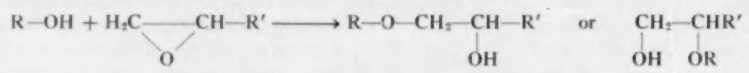
[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

is used. Little or nothing has been published on the use of such coreactant curing agents with epoxides to obtain wrinkle resistant cotton fabrics. This paper reports a study of a number of such coreactants with an epoxide on cotton and the determination of some of the textile properties of the resultant fabrics. An attempt is made to determine the type of reaction which occurs.

It is evident from the literature and from discussion at textile meetings that many workers have investigated independently a large number of inorganic catalysts for the reaction of epoxides with cotton cellulose. Unfortunately, only a small portion of these data has been published, mostly on the use of zinc fluoborate. In the present work, several acid catalysts were used in order to obtain information on their properties and for comparison of the resultant textile properties with those obtained by coreactants.

Epoxide Chemistry

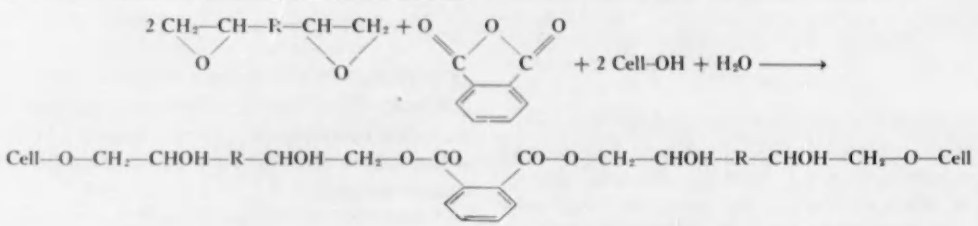
The reaction of epoxy compounds with other substances ranges from very slow to very fast depending upon the chemical nature of the coreactant, catalyst, if present, media, and other reaction conditions. For example, reaction with alcohols is slow and generally requires a catalyst; with amines and carboxylic acids the reaction is very fast and need not be catalyzed. The reaction of an epoxy compound with an alcohol to form an ether may be illustrated in the general equation



If this general case is extended to a diepoxide, reaction with two moles of alcohol can take place to form a diether. Similarly, a diepoxide finishing agent can be used to react with the polyhydric alcohol, cellulose, to cross-link the chains and impart wrinkle resistance.

In addition to cross-linkage of the cellulose chains, polymerization of the diepoxide is possible. The nature of the catalyst selected for the treatment will greatly influence the course of the reaction, as has been shown with mixtures containing an epoxy compound, an alcohol, and various catalysts [14].

More complex reactions are encountered when coreactants rather than a true catalyst are employed to cure an epoxide. With such materials certain weaknesses may be unavoidably built into the product and the stability of the cross-link may be poor. For example, in finishing cotton with an epoxy compound with phthalic anhydride as the curing agent, ester linkages which were base sensitive [11] were apparently incorporated into the finish. The following type of reaction may have occurred



This is one possibility out of a number of reactions which may occur with anhydrides, polyalcohols, and a diepoxide [14]. Organic acids should react in a manner analogous to the anhydrides. Similarly, a curing agent might be incorporated into the finish which would have sites for retention of chlorine. Thus, the curing agent, whether it is a true catalyst or a coreactant, must be carefully chosen with the end-use of the product and possible hazards of its use-life clearly in mind.

Materials and Methods

A number of curing agents were used with a commercially available diepoxide which consisted principally of 1,3-diglycidylglycerol. The fabric employed was a desized, caustic-boiled and bleached 80 × 80 white cotton print cloth, 3.2 oz./yd.[2]

Treatments, in general, were carried out as follows. A swatch of fabric was padded with a solution of the epoxide and curing agent to a wet pickup of

about 80%. Unless otherwise noted, the pad bath solutions were prepared with a 1:1 mixture (by weight) of isopropanol and water as solvent. The epoxide was completely soluble in this mixed solvent, thus eliminating the necessity of an emulsifier. The impregnated fabrics were mounted on pin frames at original dimensions, dried 7 min. at 60° C. and cured 3 min. at 180° C. in an electric oven with circulating air. Following the curing step, samples were washed with a solution (about pH 10) of approximately 0.03% of a nonionic detergent of the alkylarylpolyether alcohol type at 40° C. The samples were then ironed dry and air-equilibrated.

Physical testing was performed by standard methods at 70° F. and 65% RH. Crease recovery angles were determined on the Monsanto Tester [1a]; tearing strengths by the falling pendulum (Elmendorf) method [1b].

Results and Discussion

The use of polyvinyl alcohol to emulsify a difficultly soluble fraction of 1,3-diglycidylglycerol for application to cotton has been recommended [15]. The properties obtained by treatment of cotton print cloth with various concentrations of diepoxide–zinc fluoborate–polyvinyl alcohol, as compared with those of a fabric treated with various concentrations of a typical N-methylol finishing agent, dimethylol ethyleneurea (DMEU), with zinc nitrate catalyst, are shown in Figure 1. Concentrations of cross-linking agents were varied from 2% to 20%, with the ratio of diepoxide:zinc fluoborate:polyvinyl alcohol maintained at 20:1:1 and the ratio of DMEU:zinc nitrate at 20:1. Samples were impregnated to about 80% wet pickup, dried at 60° C. for 7 min., cured at 160° C. for 4 min., and washed.

The tearing strength retained by the fabric is plotted against the crease recovery angle. The epoxide-treated fabrics were not as strong as DMEU-treated samples at equal crease recovery angles. (More recent work at this laboratory indicates that other conditions of diepoxide application may result in fabrics with more favorable strength properties.)

Extrapolation of the curves in Figure 1 to the crease recovery angle of untreated fabric, assuming continued linearity, would show that DMEU-treated fabric would have about 5% loss in tearing strength as compared to about 50% loss with the diepoxide treatment. This appears to indicate that the greater strength loss in the diepoxide treatment is due to

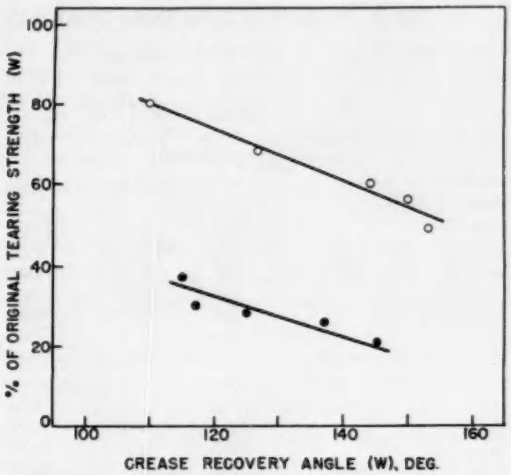


Fig. 1. Comparison of the relationship of tearing strength and wrinkle resistance of cotton print cloth treated with dimethylol ethyleneurea–zinc nitrate (○) and with diepoxide–zinc fluoborate–polyvinyl alcohol (●).

greater degradation of cellulose, presumably through acidic degradation, which is superimposed on the cross-linking effects. The small amount of degradative action with a DMEU finish, as indicated here, has been reported previously [4]. Degradation with DMEU is, in fact, reportedly less than that caused by the zinc nitrate catalyst alone under these conditions because of partial neutralization of acidity by the nitrogenous agent. The acidity developed by the zinc fluoborate catalyst is, apparently, neutralized to a lesser extent by the diepoxide. It appears that with this catalyst high acidity is necessary for the cellulose–diepoxide reaction.

To determine whether other coreactants or catalysts would provide a better strength–wrinkle resistance relationship for epoxide treatment, this study was undertaken. The effect of the polyvinyl alcohol emulsifier, which produces stiffening of the fabric and may thus reduce tearing strength, was eliminated by employing an isopropanol–water mixture as solvent for the epoxide pad baths. The use of the isopropanol–water solvent thus made possible determination of the properties imparted by the epoxide–catalyst systems without the modifying effects of softeners, stiffeners, emulsifiers, or other additives.

Screening of Coreactant Curing Agents

Several types of potential curing agent were screened. They were used in a pad bath solution

TABLE I. Properties of Cotton Fabric Obtained by Treatment with a Diepoxide and Various Curing Agents*

Curing agent	Add-on, %	Crease recovery angle (W+F), deg.	Tearing strength (W+F), g.
Untreated cotton	—	173	1963
Aluminum sulfate			
0.08%	1.1	181	1320
0.25%	5.8	247	834
0.41%	7.8	275	660
0.58%	8.8	276	547
0.74%	8.8	273	400
1-Aminoethyl-2-methyl-imidazoline			
1%	7.6	225	913
3%	12.5	241	1194
5%	15.8	229	1186
7%	17.2	210	1220
9%	19.0	191	1293
Benzoic acid			
1%	1.1	189	1187
9%	1.3	188	1167
Citric acid			
1%	2.7	178	1060
3%	7.6	226	826
5%	11.1	248	880
7%	12.1	242	873
9%	14.0	248	826
1-Hydroxyethyl-2-alkyl-imidazoline†			
1%	5.0	191	913
3%	8.3	218	900
5%	11.1	232	933
7%	13.6	235	953
9%	15.1	243	1013
Magnesium perchlorate			
0.33%	2.5	207	1253
0.67%	6.6	260	853
1%	8.1	268	720
3%	10.2	264	660
5%	9.7	286	626
7%	10.0	285	593
9%	10.1	288	646
Maleic anhydride			
1%	4.3	189	920
3%	9.4	224	763
5%	9.7	219	627
7%	9.8	216	507
9%	10.4	226	420
Oxalic acid			
2.1%	7.1	218	487
3.6%	4.3	199	320
5.0%	4.4	195	203
Phthalic anhydride			
1%	2.2	209	1126
3%	6.1	226	934
5%	8.6	245	926
7%	9.6	247	893
9%	7.6	217	853
Potassium sodium tartrate			
0.15%	1.5	210	937
0.43%	2.7	225	814
0.71%	3.6	239	780
0.99%	3.9	231	780
Potassium thiocyanate			
1%	7.3	230	813
3%	9.1	254	994
5%	8.6	234	1160
7%	10.3	221	1187
9%	12.7	199	1180
Pyromellitic dianhydride			
1%	4.4	196	967
2%	10.4	245	787
3%	12.3	255	874
4%	14.7	247	800
5%	14.9	249	733
Sodium carbonate			
0.5%	5.4	232	713
Sodium sulfite‡			
1%	7.2	248	693
3%	9.0	255	700
5%	5.9	220	826
Sodium thiosulfate			
0.6%	1.6	201	1007
1.9%	3.3	234	840
3.2%	3.3	228	807
4.5%	5.1	253	753
5.7%	6.0	254	747
Tartaric acid			
1%	4.0	216	887
3%	10.6	243	720
5%	14.1	255	734
7%	14.8	265	593
9%	15.7	239	453

* Fabric impregnated with a solution containing 16% diepoxide and the indicated concentration of curing agent (based on weight of solution), dried at 60° C. for 7 min. and cured at 180° C. for 3 min. Solutions prepared with 1:1 isopropanol : water mixture as solvent.

† This material is a mixture in which the alkyl substituents are C_{11}, C_{13}, C_{15}, and C_{17} chains.

‡ Because of solubility difficulties, it was necessary to employ 1:2 isopropanol : water mixture as solvent in this set.

TABLE I.—*Continued*

Curing agent	Add-on, %	Crease recovery angle (W+F), deg.	Tearing strength (W+F), g.
Triethanolamine			
1%	1.8	181	956
3%	4.9	204	880
5%	6.2	201	887
7%	8.0	214	893
Trimellitic anhydride			
1%	3.0	182	1074
3%	10.3	246	813
5%	13.9	244	900
7%	17.6	237	722
Urea phosphate			
3.2%	5.3	210	960
4.4%	7.4	225	913
5.7%	8.4	221	914
Zinc fluoborate			
0.16%	1.2	183	1100
0.48%	6.1	248	733
0.80%	10.6	273	580
1.12%	9.8	279	580
1.44%	10.3	283	580
Zinc nitrate			
0.65%	2.6	201	1220
1.95%	4.9	215	1053
3.25%	6.4	219	886
4.55%	8.7	225	673
5.85%	8.8	231	626

containing 16% of the diepoxide. (A sample treated with the diepoxide alone had no add-on or improvement in crease recovery angle.) Among the curing agents tried were organic acids and anhydrides, salts of strong mineral acids, basic salts, and substituted amines. The results obtained in these experiments are listed in Table I. The best crease recovery angles (>270°) were obtained using zinc fluoborate, magnesium perchlorate, and aluminum sulfate as catalysts. The tearing strengths associated with these samples were, however, relatively low. These data also may be contrasted with those for the DMEU–zinc nitrate treatment shown in Figure 1.

Referring again to Table I, it can be seen that an intermediate level of wrinkle resistance (240–270°) was obtained using a number of catalysts or coreactants. These included phthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, citric acid, tartaric acid, potassium thiocyanate, sodium thiosulfate, sodium sulfite, and the two imidazoline derivatives. When the last four of these were used, varying degrees of yellowing developed on the fabrics after curing. Such yellowing is usually obtained when alkaline agents are used as catalysts in the pad–dry–cure system of finishing. Often this color can be removed by bleaching, but in some cases the yellowing is difficult or impossible to discharge.

The other agents used produced a lower level of wrinkle resistance (<240°). In many cases extremely low tearing strengths were associated with these poor crease recovery angles. Curing agents which fell into this class included oxalic acid, benzoic acid, maleic anhydride, zinc nitrate, sodium carbonate, potassium sodium tartrate, and triethanolamine. It is interesting to note that zinc nitrate, which is one of the preferred catalysts for finishing cotton with N-methylol agents, produced relatively poor crease recovery angles with severe strength losses when used with the diepoxide finishing agent.

Wide differences are noted in the add-on achieved with the various curing agents. Efficiency cannot be calculated in the usual manner from add-on and pad bath concentrations since many of the materials used are capable of reaction with the diepoxide finishing agent. Such reactions must have taken place in many cases since an add-on of about 12.8% (80% pickup of 16% finishing agent) would represent 100% finishing efficiency. Therefore, many of the materials tried were actually functioning as coreactant curing agents. That is, they both catalyzed the reaction and actually became a part of the final product. A cursory examination of the add-ons would place the organic acids and anhydrides and the imidazoline derivatives in this class. Analyses of fabrics treated with potassium thiocyanate, sodium thiosulfate, sodium sulfite, and an imidazoline derivative indicate all to be coreactants. These analyses, recorded in Table II, show that an appreciable

TABLE II. Analyses of Cotton Fabric Treated with Diepoxide and Coreactant Curing Agents

Treatment	Add-on, %	Analyses: % Sulfur	Analyses: % Nitrogen
16% Diepoxide with:			
9% Potassium thiocyanate	12.7	1.06	0.22
5% Sodium thiosulfate	10.5	0.86	—
3% Sodium sulfite	9.0	0.55	—
7% Imidazoline derivative*	13.6	—	0.50

* 1-Hydroxyethyl-2-alkyl-imidazoline.

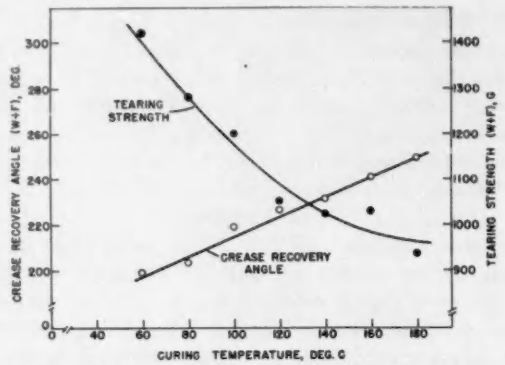


Fig. 2. Effect of curing temperature on the wrinkle resistance and tearing strength of cotton fabric finished with diepoxide, using phthalic anhydride as coreactant curing agent.

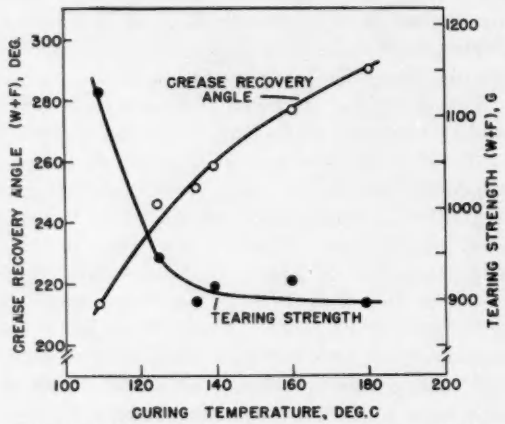


Fig. 3. Effect of curing temperature on the wrinkle resistance and tearing strength of cotton fabric finished with diepoxide, using magnesium perchlorate as catalyst.

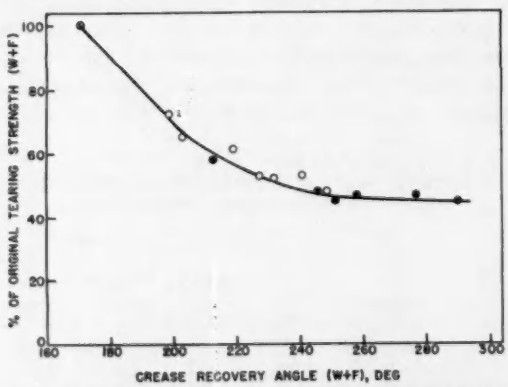


Fig. 4. Relationship of tearing strength and wrinkle resistance of cotton print cloth treated with diepoxide–phthalic anhydride (○) and with diepoxide–magnesium perchlorate (●). Untreated cotton (⊗) also is shown.

portion of the curing agent (from about 11% to 44% of the add-on) is firmly bound. However, the molar ratio of nitrogen to sulfur is considerably less in the finished fabric than in potassium thiocyanate. Some advantages and disadvantages of this type of curing agent will be discussed later in the paper.

Although not listed in Table I, four other materials were investigated for epoxide finishing catalysis. They were the boron trifluoride complexes of urea, ethylamine, triethanolamine, and piperidine. Fabric samples treated with these complexes as catalysts had very low add-ons and were not tested for physical properties.

Change in Curing Temperature

The effect of curing temperature on the wrinkle resistance and tearing strength of diepoxide-treated cotton when phthalic anhydride was used as the curing agent is illustrated in Figure 2. Using a pad bath containing 16% diepoxide and 7% phthalic anhydride, samples were impregnated, dried at 60° C. for 7 min., and then cured at temperatures of from 60° to 180° C. for 3 min.; add-on ranged from 0.4% to 10.2%. Crease recovery angle increased smoothly as a function of the curing temperature over the entire range studied; tearing strength decreased with increasing temperature. Apparently the cotton was not esterified by the anhydride under these conditions, because fabric treated with phthalic anhydride alone at these temperatures had no add-on and no increased wrinkle resistance.

The wrinkle resistance and tearing strength of samples treated with 16% diepoxide and 3% magnesium perchlorate catalyst [2] and cured at 110° to 180° C. are shown in Figure 3. Add-on varied from 3.0% at the lowest temperature to 10.5% at the highest. The values obtained for both wrinkle resistance and tearing strength were considerably higher than those reported in Table I at the same temperature of curing (180°). The crease recovery angle is a direct function of curing temperature at the temperatures studied, while the tearing strength loss is not a linear function at curing temperatures above 125° C.

The relation of crease recovery angle to tearing strength retention for cloth of the above series of

[2] Although magnesium perchlorate is an efficient acidic catalyst for laboratory experimentation with epoxides, extreme caution must be exercised in the handling and use of this potentially explosive material. It may be unsuitable for large-scale use.

treatments is shown in Figure 4. The same relationship between the two parameters exists in both series. In Figure 4, the curve tends to swing toward higher strength at lower crease recovery angles. This would be expected, as the lower curing temperatures used to obtain the lower recovery angles would cause less cellulose degradation.

Variation of Diepoxide:Catalyst Ratio

The influence on fabric properties of additional variations in concentration of both diepoxide and catalyst—zinc fluoborate or magnesium perchlorate—is shown in Table III. These data, together with those shown for these two catalysts in Table I, cover a broad range of catalyst:diepoxide ratios. At constant catalyst:diepoxide ratio, add-on and wrinkle resistance increase as the finishing agent concentration is increased; tearing strength varies inversely with concentration. As diepoxide concentration is increased with constant catalyst concentration, add-on is increased, but with less pronounced increase in wrinkle resistance. With zinc fluoborate catalyst, the tearing strength remains practically constant over the range studied. The same is generally true for magnesium perchlorate catalyst except at the highest diepoxide concentration, which produced a drastic strength change. Referring to Table I, at constant diepoxide concentration, increasing the catalyst:diepoxide ratio brought about increased add-on and wrinkle resistance. These reached a plateau at a ratio characteristic of the catalyst. Past this critical catalyst concentration changes in tearing strength were not marked.

Evidence of Coreaction

In a previous paper [11], the authors have observed that a cotton fabric treated with diepoxide and phthalic anhydride could not be aftermercerized without almost complete loss of the wrinkle resistance which had been imparted by the treatment. This alkali-instability was attributed to ester linkages in the finish, and infrared curves (Figure 5) run on such samples by the KBr disc method, as described by O'Connor and coworkers [10], lend support to this hypothesis. The carbonyl band shows up strongly at 5.8 μ, indicating the presence of phthalic anhydride residues in the finish. This band was completely removed when the sample was after-

TABLE III. Effect of Additional Changes in Diepoxide and Catalyst Concentrations on Fabric Properties

Treating solution					
% Diepoxide	Catalyst con., %	Ratio by wt. cat.:diepoxide	Add-on, %	Crease recovery angle (W+F), deg.	Tearing strength (W+F), g.
	$Zn(BF_4)_2$				
8	0.4%	1:20	3.6	228	813
12	0.6%	1:20	6.2	248	653
16	0.8%	1:20	9.3	274	600
20	1.0%	1:20	12.1	280	600
24	1.2%	1:20	16.0	292	580
12	0.8%	1:15	7.2	253	640
16	0.8%	1:20	10.4	267	614
20	0.8%	1:25	12.3	275	607
24	0.8%	1:30	12.8	270	626
30	0.8%	1:35	18.1	303	600
	$MgClO_4$				
8	1.5%	1:5.33	4.5	255	814
12	2.25%	1:5.33	7.7	275	767
16	3.0%	1:5.33	10.2	284	773
20	3.75%	1:5.33	13.6	297	807
24	4.5%	1:5.33	16.6	294	553
12	3%	1:4	8.0	280	667
16	3%	1:5.33	11.3	286	740
20	3%	1:6.67	14.1	302	706
24	3%	1:8	16.6	300	633
30	3%	1:10	20.3	298	480

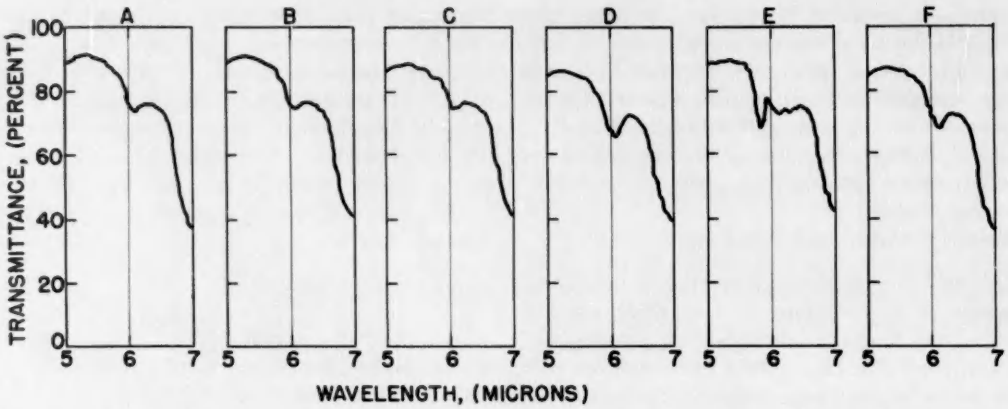


Fig. 5. Segment of infrared absorption curves showing the 5–7 μ wavelength region for: A, untreated cotton; B, mercerized cotton; C, cotton treated with diepoxide–zinc fluoborate; D, cotton treated with diepoxide–zinc fluoborate and aftermercerized; E, cotton treated with diepoxide–phthalic anhydride; and F, cotton treated with diepoxide-phthalic anhydride and aftermercerized.

mercerized. A sample treated with diepoxide in the presence of zinc fluoborate catalyst instead of phthalic anhydride exhibited no absorption at this band and was essentially unchanged by aftermercerization.

Dyeing Properties

Among the catalysts studied and reported in Table I are a number capable of coreaction. Swatches of selected samples were subjected to a test of their response to direct, disperse, acid, and basic dyes (Table IV). These dyeings give some indication of the nature of the finish. For example, only the sample treated with diepoxide and 1-hydroxyethyl-2-alkyl-imidazoline was fully receptive to the direct dye. Thus, this sample was significantly different from the others, probably due to the chemical constitution of the finish. Samples treated with the strong acid catalysts either resisted the direct dye or were only slightly dyed, probably due to cross-linkage of the cellulose.

TABLE IV. Response to Four Classes of Dyes of Cotton Fabric Treated with Diepoxide Using Various Curing Agents

Curing agent used in treatment	Crease recovery angle,* deg.	Response to dyeing†			
		Direct dye‡	Disperse dye**	Acid dye††	Basic dye‡‡
None (untreated cotton)	173	++	−	−	0
Aluminum sulfate	275	−	−	0	+
Citric acid	248	−	−	−	+
1-Hydroxyethyl-2-alkyl-imidazoline	243	++	+	++	0
Magnesium perchlorate	290	0	+	−	−
Phthalic anhydride	266	−	+	−	+
Potassium thiocyanate	254	+	−	+	−
Pyromellitic dianhydride	255	+	−	−	+
Sodium carbonate	232	+	0	−	+
Sodium sulfite	255	−	0	0	++
Sodium thiosulfate	266	−	0	0	++
Tartaric acid	243	−	−	−	+
Trimellitic anhydride	244	−	+	−	+
Zinc fluoborate	274	−	−	−	−

* Crease recovery angle is included to identify sample (Table I) and indicate degree of cross-linkage.
† Response to dyeing rated as follows: 0 = resist; − = slight; + = moderate; and ++ = intense.
‡ 2% dyeing with Pontamine Fast Red 8 BNL (C.I. 28160).
** 2% dyeing with Eastone Fast Red N-GLF (Disp. Red. 35).
†† 2% dyeing with Kiton Red 3 GLL.
‡‡ 2% dyeing with Methylene Blue Chloride (C.I. 52015).

TABLE V. Durability of Wrinkle Resistance of Cotton Fabrics Treated with Diepoxide and Various Curing Agents

Curing agent	Crease recovery angle (W+F), degrees			
	Originally	After phosphoric acid–urea stripping*	After treatment at pH 3†	After treatment at pH 11‡
Aluminum sulfate	252	254	249	253
Citric acid	233	242	243	214
1-Hydroxyethyl-2-alkyl-imidazoline	258	228	240	254
Magnesium perchlorate	278	276	278	276
Phthalic anhydride	239	235	246	211
Potassium thiocyanate	242	239	229	230
Sodium sulfite	234	220	217	237
Sodium thiosulfate	244	230	231	243
Trimellitic anhydride	248	244	241	221
Zinc fluoborate	260	259	264	264

* Treated with 1.5% *ortho*-phosphoric acid–5% urea at 80° C. for 30 min.
† Treated with buffer solution, pH 3.0, at 40° C. for 30 min.
‡ Treated with 1% sodium carbonate, pH 11, at 80° C. for 1 hr.

Moderate response to the disperse dye was observed on samples treated with four of the catalysts. Two of these were anhydrides, from which one would expect to produce ester linkages.

The only strong response to the acid dye was obtained on the sample treated with 1-hydroxyethyl-2-alkyl-imidazoline catalyst. With coreaction, the finish would contain tertiary amine groups and thus be basic.

The basic dye produced the broadest range of responses in the treated cottons. The untreated control was completely resistant as was the above mentioned basic finish from the diepoxide and the imidazoline derivative. The other swatches varied in their receptivity to the dye, the finishes catalyzed by sodium sulfite and by sodium thiosulfate being the most intensely dyed.

Durability of Finish

To broaden these interpretations, the durability of the wrinkle resistance of a number of the finishes to phosphoric acid-urea stripping, to souring at pH 3, and to hydrolysis at pH 11 was determined (Table V).

In general, the finishes showed the outstanding durability characteristic of this diepoxide. However, finishes obtained with citric acid, phthalic anhydride, and trimellitic anhydride as curing agents exhibited poorer durability to alkaline hydrolysis than the finishes produced with the other catalysts. This indicates the presence of alkali-unstable groups in the cross-linkages, probably ester linkages.

Treatment at a pH of 3 did not have the serious effect with these finishes that is usually observed with finishes based on N-methylol agents. Finishes produced with the diepoxide and alkaline agents were poorer in their resistance to the treatment at pH 3 than those produced by other agents. Resistance of all the finishes to the hot phosphoric acid treatment was outstanding. The greatest loss of wrinkle resistance with this stripping technique was in the case of the finish produced with the imidazoline derivative as curing agent and was only 30°.

Pad Bath Additives

Improvement in properties of wrinkle resistant cottons can often be achieved by the use in the treatment of additives such as acrylic polymers [17], polyethylene [12], or silicones [16]. This is mainly a physical effect due to changes in surface characteristics. As a matter of interest, a representative of each of these types was used in 16% diepoxide–0.8% zinc fluoborate treatment. The additive was incorporated into the pad bath and finishing carried out as in the previously described experiments. In each case, both crease recovery angle and tearing strength were improved. With polyethylene, for example, the angle was improved from 253° to 287° and the tearing strength from 646 g. to 854 g.

Summary and Conclusions

Curing agents, both catalyst and coreactant types, for promoting the reaction of a diepoxide, 1,3-diglycidylglycerol, with cotton to produce wrinkle-resistant textiles have been studied. It was found that coreactant curing agents generally produced a lower

degree of wrinkle resistance and correspondingly smaller loss of strength than resulted with the use of acid catalysts. Apparently, the relationship between crease recovery and tearing strength is not affected no matter whether an acid catalyst such as magnesium perchlorate or a coreactant such as phthalic anhydride is used with the diepoxide. The coreactants introduced linkages and chemical groups which are not present when a true catalyst is used with the diepoxide agent. This resulted in changed dyeing characteristics and changed resistance to certain reagents. Coreaction with phthalic anhydride was investigated more extensively than with other coreactant curing agents and it was found that considerable reaction occurred at low temperatures with wrinkle resistance and add-on increasing with higher temperatures. Apparently an ester group was introduced in the cross-link, as shown by infrared curves before and after exposure of the finish to strong alkali.

Chemical analyses of fabric treated with diepoxide and potassium thiocyanate, sodium sulfite, sodium thiosulfate, or an imidazoline derivative showed that these materials are coreactant curing agents.

For comparison, several acid catalysts were used. It was found that strongly acid magnesium perchlorate and aluminum sulfate produced finishes with wrinkle resistance equivalent to that of finishes catalyzed by zinc fluoborate. Equivalent wrinkle-resistance–strength relationships also existed. However, these substitute catalysts do have the advantage of not releasing volatile fluorides while curing the finish on the fabric. Magnesium perchlorate, however, must be handled with extreme caution.

Tearing strength and wrinkle resistance can be improved by use of a silicone, acrylic polymer, or polyethylene additive.

Acknowledgments

The authors wish to express their appreciation to members of the Product Evaluation group of this Division for the many textile tests reported in this paper; to George I. Pittman for drawing the figures; to John G. Frick, Jr., for his many helpful suggestions; and to Gordon J. Boudreaux for running infrared absorption curves.

Literature Cited

1. American Society for Testing Materials, Philadelphia, Pa., ASTM Designation: (a) D1295–53T; (b) D1424–56T.
2. Benerito, R. R., Webre, B. G., and McKelvey, J. B., TEXTILE RESEARCH JOURNAL **31**, 757–769 (1961).
3. Borghetty, H. C., *Textile World* **108**, No. 4, 89 passim (1958).
4. Frick, J. G., Jr., Andrews, B. A. K., and Reid, J. D., TEXTILE RESEARCH JOURNAL **30**, 495–504 (1960).
5. Galligan, J., Sookne, A. M., Adams, J. T., Jr., Guest, H., and Lourigan, G. H., TEXTILE RESEARCH JOURNAL **30**, 208–222 (1960).
6. Lee, H. L. and Neville, K. O., "Epoxy Resins," New York, McGraw-Hill Book Co., 1957.
7. McKelvey, J. B., Benerito, R. R., Webre, B. G., and Berni, R. J., *J. Polymer Sci.* **51**, 209–230 (1961).
8. McKelvey, J. B., Webre, B. G., and Benerito, R. R., *Am. Dyestuff Reptr.* **49**, 804–809 (1960).
9. McKelvey, J. B., Webre, B. G., and Klein, E., TEXTILE RESEARCH JOURNAL **29**, 918–925 (1959).
10. O'Connor, R. T., DuPré, E. F., and McCall, E. R., *Anal. Chem.* **29**, 998–1005 (1957).
11. Reinhardt, R. M., Kullman, R. M. H., Moore, H. B., and Reid, J. D., *Am. Dyestuff Reptr.* **47**, P758–P764 (1958).
12. Reinhardt, R. M., Mazzeno, L. W., Jr., and Reid, J. D. (to U. S. A., as represented by the Sec. of Agr.), U. S. Patent 2,917,412 (December 15, 1959).
13. Schroeder, C. W., and Condo, F. E., TEXTILE RESEARCH JOURNAL **27**, 135–145 (1957).
14. Shechter, L. and Wynstra, J., *Ind. Eng. Chem.* **48**, 86–93 (1956).
15. Shell Chem. Corp., *Tech. Bull.* **SC:57-19** (1957).
16. Simpson, B. G., *Am. Dyestuff Reptr.* **46**, P991–P998 (1957).
17. Steele, R. and Browne, C. L., *Am. Dyestuff Reptr.* **45**, 525–528 (1956).

Manuscript received March 20, 1961.

Studies on the Chlorine Retention of Fabrics Treated with Dimethylol Ethylene Urea

P. C. Mehta and J. R. Mody

Ahmedabad Textile Industry's Research Association, Ahmedabad 9, India

Abstract

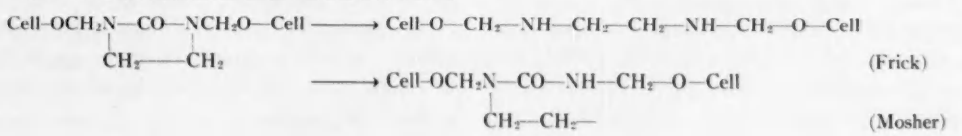
Chlorine retention and loss in strer due to scorching have been reported for fabrics treated with dimethylol ethylene urea (DMEU) under different conditions of processing and use. Since DMEU is theoretically not expected to be chlorine retentive, various mechanisms have been proposed in the literature to explain this anomaly. The present paper reports the results of studies designed to follow the chemical changes produced in DMEU under different conditions of treatment and to relate these to chlorine retention and damage. It has been shown that DMEU-treated fabrics contain varying amounts of >NH, $>NCH_2OH$ and $>NCH_2OCH_2N<$ groups under different conditions of treatment. All these groups lead to chlorine retention. The molar ratio of formaldehyde to cyclic ethylene urea (CEU) in the DMEU, the efficiency of the catalyst in promoting cross-linking with cellulose, the possibility of hydrolysis of the cross-links during storage or laundering, etc., are all factors affecting chlorine retention. Even under optimum conditions of processing and storage, changes are produced in the finish which increase considerably the damage due to chlorine retention, particularly when such a fabric is given repeated alkaline washings.

DIMETHYLOL ethlyene urea (DMEU) is used extensively in the production of crease-resistant and minimum-care cotton fabrics. Even though DMEU was introduced to the textile industry as a non-chlorine-retentive finish, it has been found from experience that fabrics treated with DMEU are not entirely free from this defect, though with proper processing they are vastly superior to the earlier finishes based on methylol derivatives of urea and melamine. The fact that DMEU, which does not contain sites for chlorine retention, should exhibit this defect has aroused considerable interest [1, 6, 12, 18, 19]. Some of the mechanisms proposed to explain the anomaly have been briefly reviewed by us in an earlier paper [11], which also gave data showing a close dependence of chlorine retention damage on the $>NCH_2OH$ content of the test fabric. The present paper is an extension of the earlier work and describes a study of the problem of chlorine retention by DMEU-treated fabrics in greater detail.

DMEU-treated fabrics show chlorine retention under the following conditions:

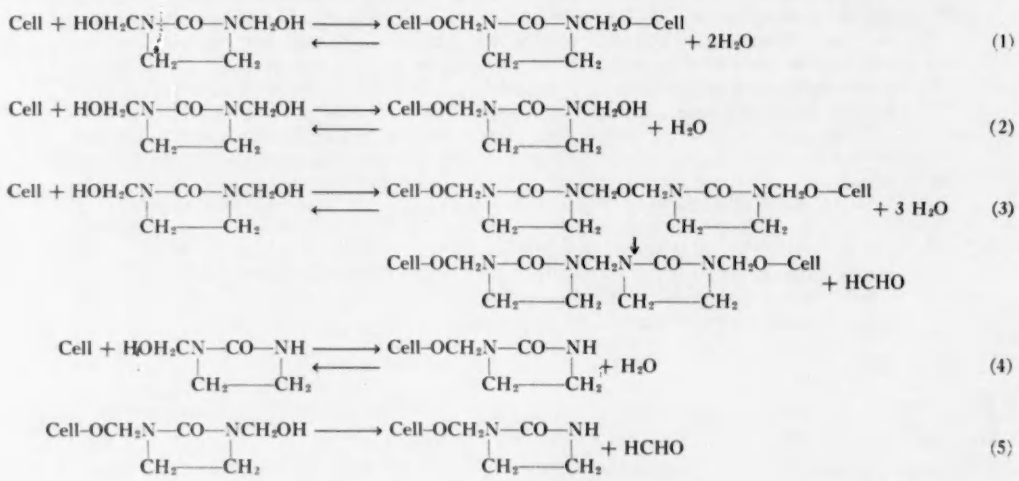
If the curing is mild or if ammonium salt catalysts are used, the finished fabric is initially chlorine retentive. The extent of chlorine retention and subsequent degradation of the fabric on scorching may be considerable under these conditions. On the other hand, well-cured fabrics with metal salt catalysts show initially low chlorine retention. This increases, however, on (a) progressive laundering, (b) storage in presence of unwashed catalyst residues, (c) steaming, and (d) acid souring.

The mechanisms proposed by Frick et al. [6] and by Mosher [12] involve a rupture of the ethylene urea ring, with the formation of imino (or amino) groups:



The cyclic ethylene urea (CEU) structure is quite stable and is hydrolyzed only by drastic treatment with alkalis or acids [8]. Doubts have been expressed about the possibility of CEU ring rupture under the mild conditions of domestic laundering [19]. According to Smith, it is not necessary at all to postulate such a rupture. Hydrolysis of the $>NCH_2O$-Cell bonds during acid souring or storage with unwashed catalyst residues and of $>NCH_2OCH_2N<$ bonds (in the DMEU polymer formed under mild curing conditions) during alkaline treatments would produce $>NCH_2OH$ groups, which would give >NH by loss of formaldehyde. It has been shown earlier [11] that $>NCH_2OH$ groups can be estimated in the DMEU-treated fabric by alkaline hydrolysis and determination of the formaldehyde evolved. Such an estimation would experimentally substantiate the mechanisms proposed by Smith.

In the treatment of cotton with DMEU, under the usual conditions, the following reactions may be expected to occur:



Reactions 1 and 2 represent formation of methylol ether linkages between DMEU and cellulose. The relative extents of these two reactions will depend on the efficiency of the catalyst in promoting the etherification reaction. Reaction 3 represents what happens when curing conditions are mild. Commercial DMEU generally shows a value of 1.7 to 1.8 for the molar ratio of formaldehyde to CEU. Thus a certain amount of monomethylol ethylene urea would be present in commercial DMEU. During curing, some decomposition of DMEU may also occur, giving the monomethylol derivative. The reaction of the latter with cellulose is shown in Equation 4. Equation 5 shows the decomposition of free $>NCH_2OH$ groups in the treated fabric to >NH during curing, as suggested by Frick et al. [6].

Thus in DMEU-treated fabrics there do exist one or more of >NH, $>NCH_2OH$, and $>NCH_2OCH_2N<$ groups, all of which are sites for either immediate or potential chlorine retention. The extent to which they exist will depend on the composition of DMEU, the cross-linking efficiency of the catalyst used, conditions of curing, and the subsequent history of the sample.

The present paper reports attempts to study these reactions when a cotton fabric was treated with DMEU under different curing conditions. Attempts have also been made to follow the chemical changes which take place in the treated fabric during storage and washing and to relate these to chlorine retention. It was hoped that an estimate of $>NCH_2OH$ and $>NCH_2OCH_2N<$ would be obtained by the alkaline hydrolysis method described earlier [11], whereas >NH groups, present initially in the fabric as well as those obtained by alkaline decomposition of $>NCH_2OH$ groups, would be determined from measurements of the equilibrium chlorine-retention values. It will be seen later in the paper that the latter aim could not be accomplished due to a complicated side reaction.

Experimental Procedure

Materials

Fabric. 38s/38s Cotton poplin, 112 ends and 72 picks/in., mercerized, bleached, and free from any finishing materials, was used. This fabric was boiled for 30 min. with distilled water and washed to a neutral pH.

DMEU. A typical, commercial product (Resloom E-50, Monsanto) was used. It gave a value of 1.74 for the molar ratio of formaldehyde to CEU and contained 1.4% free formaldehyde. It was stored at about 5° C. throughout the duration of this work.

Catalysts. Magnesium chloride hexahydrate and ammonium sulfate were selected as the most and least efficient catalysts for cross-linking. Both catalysts were of B.P. quality.

Application of DMEU. The general procedure of resin application has been described earlier in detail except that the process wash was given with 2 g./l. of anionic detergent (pH $\approx$ 7.5) [11].

Catalyst concentrations used were 2.5% ammonium sulfate and 30.0% magnesium chloride hexahydrate, both on the weight of the resin. The fabrics were cured at 110°, 130°, 160°, and 180° C., time of curing being kept constant (5 min.) in each case.

Testing. The pH of the aqueous extract of the fabric, crease recovery, tear strength, and nitrogen content of the test fabric specimens were measured by methods described earlier [10]. The conditions of hypochlorite treatment were as given in AATCC Tentative Test Method 92-1958 unless stated otherwise. Loss in tensile strength due to scorching was also determined according to this method, using a 3-in. test length, cross head speed of 5 and chart speed of 50, on an Instron tensile tester. Amount of retained chlorine was determined by the method described by Frick et al. [6].

Determination of Magnesium in Test Fabric

When required, magnesium was estimated by the use of sodium salt of ethylene diamine tetraacetic acid (EDTA), using Solochrome Black WDFA as indicator. The latter forms a wine-red complex with magnesium at pH 10. On addition of EDTA to this solution, a stronger complex of Mg^{++} with EDTA is formed changing the color of the solution from wine-red to pure blue.

Approximately 2 g. of the test fabric, accurately weighed and cut into small pieces, was boiled for 40 min. with 200 ml. of distilled water containing 6 ml. of 6 *N* nitric acid. The solution was then filtered into a 250-ml. volumetric flask. The cloth pieces were washed with boiling distilled water until the washings were free from magnesium. The filtrate and washings were made up to 250 ml., neutralized with concentrated ammonia, and the excess ammonia boiled off. The solution was then filtered and made up to 100 ml. To 25 ml. of this solution, 1 to 2 ml. of the buffer (ammonium chloride plus ammonium hydroxide; pH 10) and 4 to 5 drops of the indicator (0.5 g. Solochrome Black WDFA plus 4 to 5 g. hydroxylamine hydrochloride dissolved in 100 ml. ethanol) were added and the contents were then titrated with 0.001 *N* EDTA until a pure blue color was obtained. Magnesium has been expressed as milligrams per 100 grams of dry fabric. Further details of EDTA titrations may be obtained from standard references [5].

Determination of $>NCH_2OH$ Content

Details of the method have already been given earlier [11]. The data collected to standardize the method were not given, however, and are shown here in Table I. It is evident that, using sodium hydroxide of 0.2 to 0.5 *N* at temperatures of 35°–50° C., the formaldehyde evolution was negligible after 2 hr. This method measures formaldehyde present in the form of $>NCH_2OH$ and $>NCH_2OCH_2N<$ groups. However, no hydrolysis of $>NCH_2O$-Cell bonds is involved, a fact substantiated by the unchanged crease recovery of the fabric after alkaline hydrolysis under these conditions for 240 hr. On the other hand, with a higher alkali concentration (2 *N*) there appears to be some hydrolysis of the cross-links, judging from the progressive increase in the value of formaldehyde evolved as well as the fall in crease recovery after the alkaline hydrolysis. $>NCH_2OH$ determinations have been carried out using 0.5 *N* sodium hydroxide at 35° C. for 72 hr.

Results and Discussion

Effect of Catalyst Type and Curing Conditions

Table II gives results for fabrics treated with DMEU and magnesium chloride or ammonium sulfate catalysts at curing temperatures of 110° to 180° C. The importance of "hard" curing and the relative effectiveness of different catalysts in reducing

TABLE I. Alkaline Hydrolysis of DMEU-Treated Fabrics under Different Conditions

Catalyst	Sodium hydroxide *N*	Temperature of hydrolysis, ° C.	% Formaldehyde evolved after hydrolysis for			Crease recovery after 240 hr. of hydrolysis, deg.	
			2 hours	72 hours	192 hours	Before	After
Tartaric acid	0.18	35	0.207	0.207	0.207	—	—
	0.5	20	0.207	0.244	0.244	—	—
	0.5	35	0.207	0.207	0.207	—	—
$MgCl_2$, $6H_2O$	0.5	35	0.051	0.059	0.055	279	274
	0.5	50	0.051	0.059	0.055	279	275
	2.0	35	0.073	0.073	0.077	279	263
	2.0	50	0.051	0.083	0.089	279	272
$(NH_4)_2SO_4$	0.5	35	0.076	0.086	0.075	261	261
	0.5	50	0.081	0.086	0.086	261	262
	2.0	35	0.081	0.089	0.111	261	249
	2.0	50	0.081	0.114	0.119	261	248

chlorine retention have been studied, and the experimental data reported, by various workers [1, 4, 6, 12]. In particular, it has been observed that chlorine retention can be practically eliminated by using magnesium chloride or zinc nitrate catalysts at high curing temperatures, whereas ammonium salt catalysts even at these temperatures are not as effective in reducing chlorine retention. The data in Table II offer an explanation for these experimental observations.

With both magnesium chloride and ammonium sulfate, crease recovery increases steadily with increasing curing temperature and reaches a high value at 160° and 180° C. Tear strength shows a corresponding progressive decrease. Cooke et al. [3] obtained low crease recovery and low nitrogen content (that is, low resin fixation) with the DMEU–ammonium sulfate system at curing temperatures higher than 320° F. (160° C.). The present data are in disagreement with this observation.

Several interesting differences can be seen in the results obtained with the two catalysts. Thus alkaline hydrolysis produces a substantial decrease in the crease recovery of the fabrics cured with DMEU and magnesium chloride at 110° and 130° C. This is not the case for the corresponding samples with the ammonium salt catalyst. At the two higher curing temperatures, there is no decrease in fabric crease recovery due to alkaline hydrolysis for either catalyst. Also, the content of $>NCH_2OH$ (plus $>NCH_2OCH_2N<$) groups steadily decreases with increasing curing temperature in the case of both the catalysts. However, the decrease is much larger with the metal salt catalyst. Lastly, with the ammonium salt

TABLE II. Properties of Fabrics Treated with DMEU under Different Curing Conditions

Sample details		Crease recovery, deg.		Tear strength, g.	Free $>N\cdot CH_2OH$, %	% Chlorine retained	% Loss in strength due to scorching
		Before alkaline hydrolysis	After alkaline hydrolysis				
$MgCl_2$	110° C.	232	209	930	0.431	0.111	80
$MgCl_2$	130° C.	255	242	816	0.272	0.084	59
$MgCl_2$	160° C.	277	275	604	0.074	0.049	1
$MgCl_2$	180° C.	279	277	546	0.051	0.046	0
$(NH_4)_2SO_4$	110° C.	235	231	952	0.305	0.145	73
$(NH_4)_2SO_4$	130° C.	250	249	872	0.195	0.109	66
$(NH_4)_2SO_4$	160° C.	262	261	696	0.173	0.087	53
$(NH_4)_2SO_4$	180° C.	270	264	655	0.153	0.079	49
Blank		131	—	1396	0.000	0.000	0.20

TABLE III. Determination of Free > NH Initially Present in Fabrics Treated with DMEU under Different Curing Conditions

Sample details		Free $>NCH_2OH$*	Free $>NCH_2OH + >NH$*	Free $>NH$*
$MgCl_2$	110° C.	0.128	0.197	0.069
$MgCl_2$	130° C.	0.091	0.157	0.066
$MgCl_2$	160° C.	0.034	0.092	0.058
$MgCl_2$	180° C.	0.026	0.076	0.050
$(NH_4)_2SO_4$	110° C.	0.115	0.186	0.071
$(NH_4)_2SO_4$	130° C.	0.075	0.156	0.081
$(NH_4)_2SO_4$	160° C.	0.057	0.131	0.074
$(NH_4)_2SO_4$	180° C.	0.044	0.124	0.080

* Expressed as percent nitrogen calculated on weight of the fabric.

catalyst, chlorine retention is higher even when $>NCH_2OH$ content is lower compared to the corresponding values with the metal salt catalyst.

Mild curing with magnesium chloride appears to favor Reaction 3, involving formation of methylene ether linkages in the DMEU, to a considerable extent. Such a reaction probably best explains the large decrease in crease recovery after alkaline hydrolysis. As curing temperature increases, the methylene ether linkages are changed to $>NCH_2N<$ bonds with loss of formaldehyde (see Equation 3). Simultaneously the equilibrium in Reaction 1 shifts more and more towards the right, favoring formation of cross-links. The possibility of methylene ether formation at low curing temperatures has been postulated earlier by Reid et al. [16]. Higher values of HCHO/CEU molar ratios obtained at the lower curing temperatures also substantiate this mechanism. With ammonium sulfate, methylene ether formation does not seem to occur at the low curing temperatures. This is supported by the fact that alkaline hydrolysis of the mildly cured samples with this catalyst produces practically no fall in crease recovery. Compared to magnesium chloride, the ammonium salt catalyst produces a much smaller decrease in $>NCH_2OH$ content of the fabric with increasing curing temperature. The high $>NCH_2OH$ contents obtained with the latter catalyst at high curing temperatures can be explained if one postulates, as do Cooke et al. [3], that hydrolysis of the cellulose–DMEU cross-links assumes a significant role under these conditions. The larger proportion of $>NCH_2OH$ obtained with the ammonium salt catalyst would favor Reaction 5, leading to formation of $>NH$ groups. This would explain the higher chlorine retention with lower $>NCH_2OH$ values obtained with this catalyst as compared to those obtained with the metal salt catalyst.

It was hoped that an estimate of the $>NH$ groups initially present in the cured fabric would be obtained by alkaline hydrolysis of the $>NCH_2OH$ (plus $>NCH_2OCH_2N<$) groups followed by determination of chlorine retention. Subtracting the value for initial $>NCH_2OH$ (plus $>NCH_2OCH_2N<$) from this, one would get the initial $>NH$. To ensure a completion of the reaction between $>NH$ and hypochlorite, the reaction was carried out for 14 hr. at 25° C. with sodium hypochlorite at 9.5 pH containing 2.5 g./l. available chlorine. A 50:1 liquor ratio was used. The results obtained are shown in Table III. The values of $>NCH_2OH$ and $>NH$ are expressed in terms of percent nitrogen (on weight of fabric) for ease of computation.

The results show consistently a slightly higher value of $>NH$ in the case of the ammonium salt catalyst. Unfortunately, a complicating side reaction was observed in the prolonged treatment with hypochlorite, which prevented a more exhaustive application of this method.

TABLE IV. Effect of Storage (with Catalyst Residues) on Properties of DMEU-Treated Fabrics

Sample details		pH of unwashed fabrics	% Loss in nitrogen	Crease recovery		Free $>NCH_2OH$, %		% Chlorine retained	% Loss in strength due to scorching	Yellowness of scorched fabric*
				Original	Stored	Original	Stored			
$MgCl_2$	110° C.	6.8	00	233	178	0.431	0.354	0.253	86	III
$MgCl_2$	130° C.	6.8	32	255	188	0.272	0.392	0.285	87	III
$MgCl_2$	160° C.	6.3	35	277	228	0.074	0.338	0.239	85	II
$MgCl_2$	180° C.	6.0	25	279	231	0.051	0.324	0.229	80	II
$(NH_4)_2SO_4$	110° C.	5.7	17	235	165	0.305	0.155	0.153	84	I
$(NH_4)_2SO_4$	130° C.	5.2	12	250	181	0.195	0.228	0.153	84	I
$(NH_4)_2SO_4$	160° C.	5.3	21	262	195	0.173	0.239	0.177	78	I
$(NH_4)_2SO_4$	180° C.	5.4	22	270	206	0.153	0.267	0.173	83	I–II

* I, light yellow; II, medium yellow; III, heavy yellow-brown.

Effect of Storage

It has been reported that in the United States it is not uncommon to omit the process wash which should normally be given to the resin-treated fabric after curing. The adverse effects of this practice have been stressed in a number of publications. Thus Bacon et al. [1] state that a neutralizing wash after curing is essential for obtaining the maximum resistance to chlorine damage, especially after laundering, from DMEU-treated fabrics. Mosher [12], Smith [19], and Reid et al. [17] have also published data showing the increased chlorine damage to DMEU-treated fabrics if these are stored without washing off the catalyst residues.

Table IV gives data for various DMEU-treated fabrics which were stored for five months under ordinary laboratory conditions, leaving the catalyst residues unwashed. The pH of the fabric was determined on the stored and unwashed fabric whereas the rest of the determinations were done after washing the stored fabrics with 2 g./l. anionic detergent (pH $\approx$ 7.5). It can be seen that all the fabrics show an acidic pH, except the two mildly cured samples with magnesium chloride catalyst, which are almost neutral. Fabric pH is more acidic when ammonium sulfate was used as catalyst. This would be expected.

The data show that when DMEU-treated fabrics are stored without washing for a long time they lose a substantial proportion of the resin, and consequently crease recovery, as soon as they are given a wash. The high loss of nitrogen content and of crease recovery clearly point to an extensive hydrolysis of the DMEU–cellulose cross-links that occurs during storage with catalyst residues. In addition, $>NCH_2OH$ content has also generally shown an increase. This increase is greater as the degree of cross-linking during curing increases. Thus it is higher with the metal salt catalyst and with increasing curing temperature. During storage with the catalyst residues, one expects Reaction 1 to continue albeit at a much slower rate. Formation of fresh cross-links as well as hydrolysis of existing cross-links would go on simultaneously, and their relative extents would depend on the relative proportions of the reactants and products. The greater the degree of cross-linking in the cured fabric, the greater would be the hydrolysis during storage and therefore the larger the increase in $>NCH_2OH$. Removal of the resin, hydrolyzed at both ends, from the system during washing with the consequent loss of $>NCH_2OH$ groups formed due to hydrolysis, complicates the picture. To eliminate this complication, two fresh samples of the fabric were treated, as usual, with DMEU and magnesium chloride and cured at 110° and 180° C. respectively. These were stored as before with the catalyst residues unwashed for periods of one and two months. Free methylol content was determined on these samples without giving them a wash. The results are given below:

Cured at	$>NCH_2OH$ content after storage for		
	0*	1 month	2 months
110° C.	1.364	1.458	1.536
180° C.	0.114	0.365	0.511

* A different commercial DMEU sample was used for this treatment giving different initial $>NCH_2OH$ values.

These data support the mechanism, postulated above, of the formation and hydrolysis of cross-links occurring simultaneously in DMEU-treated samples stored in an unwashed state.

Chlorine retention and loss in strength due to scorching both show tremendous increases, and even the two fabrics (magnesium chloride catalyst, curing at 160° and 180° C.) which were initially chlorine resistant are completely unsatisfactory after storage.

Table V shows what happens when the same fabrics are stored after a proper process-wash. The finishing treatments and conditions and duration of storage were the same as for the fabrics in Table IV. The results, as expected, are very different. The pH of all the fabrics is slightly alkaline and crease recovery is not affected at all. Surprisingly, even in the absence of any acidity in the stored fabrics, $>NCH_2OH$ content has increased appreciably in all cases, with a corresponding increase in chlorine retention and strength loss after scorching. These results are in contradiction to the accepted theory of the chlorine resistance of DMEU-treated fabrics, cured with magnesium chloride at high temperatures, even under proper conditions of processing and storage. For example, the two fabrics cured with this catalyst at 160° and 180° C., respectively, show an initial chlorine damage (that is, strength loss after scorching due to retained chlorine) of 1% and 0%, which increases after storage to 31% and 11%. These latter results are misleading, however, because in the single treatment with hypochlorite recom-

TABLE V. Effect of Storage on Properties of DMEU-Treated Fabrics (after a Process-Wash)

Sample details	pH of fabric	Crease recovery		Free > NCH_2OH, %		Before alkaline hydrolysis		After alkaline hydrolysis	
		Original	Stored	Original	Stored	% Chlorine retained	% Loss in breaking strength due to scorching	% Chlorine retained	% Loss in breaking strength due to scorching
$MgCl_2$ 110° C.	8.9	232	238	0.431	0.824	0.233	84	0.587	91
$MgCl_2$ 130° C.	8.8	255	258	0.272	0.737	0.195	74	0.555	90
$MgCl_2$ 160° C.	8.6	277	274	0.074	0.332	0.097	31	0.282	76
$MgCl_2$ 180° C.	8.3	279	286	0.051	0.255	0.070	11	0.208	60
$(NH_4)_2SO_4$ 110° C.	8.6	235	240	0.305	0.732	0.219	78	0.538	89
$(NH_4)_2SO_4$ 130° C.	8.2	250	256	0.195	0.614	0.191	76	0.492	90
$(NH_4)_2SO_4$ 160° C.	7.5	262	271	0.173	0.563	0.156	68	0.421	89
$(NH_4)_2SO_4$ 180° C.	7.5	270	267	0.153	0.483	0.159	71	0.361	88

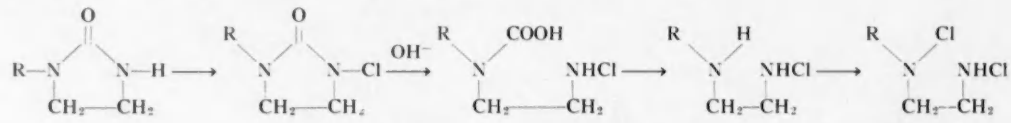
mended in the AATCC test only a fraction of the $>NCH_2OH$ is converted to $>NH$ and then to $>NCl$. It is only after repeated mild alkaline washing (as given in laundering) that the reaction $>NCH_2OH \rightarrow >NH + HCHO$ reaches completion and the full extent of chlorine damage is realized. This condition is simulated by alkaline hydrolysis of the stored samples followed by the standard chlorine-retention test. The strength loss obtained reaches the alarming figures of 76% and 60% percent, respectively.

The increase in $>NCH_2OH$ content of carefully processed, DMEU-treated fabrics stored, after washing, in a slightly alkaline condition has been repeatedly observed in this laboratory during the course of this work. Probably, an uncatalyzed hydrolysis of the cellulose–DMEU cross-links occurs due to water always present in cotton at ambient conditions. Mosher's [12] observation that steaming of well-cured and rinsed, DMEU-finished cotton goods increases the damage due to chlorine retention lends support to the possibility of such uncatalyzed hydrolysis. A rough calculation shows that approximately 10% to 15% of the cross-links are hydrolyzed. With 5% to 6% add-on of DMEU, such a hydrolysis may not affect crease recovery, but the consequences of this phenomenon in terms of chlorine damage are very serious indeed.

Effect of Washing

The changes produced in the properties of DMEU-treated fabrics by washing, particularly in chlorine retention, have naturally been studied by many investigators under a variety of washing conditions. Mosher [12] states that a well-cured fabric will withstand repeated mild home laundering, but at higher temperatures (160° F.) or under conditions of commercial laundering, the CEU structure breaks down (cf. Introduction) leading to increased chlorine retention. Borghetty [2] also suggests a similar breaking of the ring structure. Bacon et al. [1] find that by choice of proper conditions of curing, damage due to chlorine retention can be completely eliminated even after 10 home launderings. Frick et al. [6] have reported increased chlorine retention after five high-temperature launderings as prescribed in AATCC Test 14-53. The explanation offered by them has also been mentioned earlier in this paper. In a later paper [7] they find similar increased chlorine damage after alkaline hydrolysis of DMEU-treated fabrics with 1% sodium carbonate at 80° C. for 1 hr. The corresponding 6-membered homologues of DMEU, *viz.*, the pyrimidinone derivatives, gave much lower chlorine damage, which, according to the authors, is due to the greater stability of the 6-membered ring to hydrolysis. Petterson [14] favors Frick's mechanism in preference to Mosher's, which he considers unlikely from the known chemistry of imidazolidinones. Enders and Pusch [4] have observed increased chlorine retention after laundering DMEU-treated fabrics at the boil and have concluded that temperature of laundering is the most critical factor. In considering these mechanisms involving a rupture of the CEU ring, one should bear in mind Hofmann's statement [8] that the imidazolidinone structure is very stable and

breaks down only under drastic action of alkalis and acids. Whether the alkaline treatments investigated by the various authors referred to above can be considered sufficiently drastic to rupture the CEU ring structure is open to question. On the other hand, an N-chloroimidazolidinone ring will be much less stable and will probably undergo the following reactions:



A similar reaction involving hydantoins has been reported by Petterson and Grzeskowiak [15] at pH 9. Such a reaction would affect that fraction of DMEU which has reacted with, but not cross-linked, cellulose and may explain the increased chlorine retention of DMEU-treated fabrics on treatments with hypochlorite and alkali. A more detailed study of the stability of CEU certainly seems desirable.

Table VI gives some data on the effect of mild laundering on the chlorine retention and strength loss due to scorching of DMEU-treated fabrics. The increase in chlorine damage after such a laundering is very small in practically all the samples. There is a decrease in the $>NHC_2OH$ content of all the fabrics after laundering, due to the slow conversion of these groups to >NH under the weakly alkaline conditions. This change increases the rate of chlorine uptake in the subsequent hypochlorite treatment, as can be seen from the results on chlorine retention. However, where the original content of $>NCH_2OH$ is low, the increased chlorine retention is not large enough to produce significantly higher strength loss due to scorching. On the other hand, when the initial $>NCH_2OH$ content is high, the strength loss due to scorching is so large to start with that the scope for further strength loss due to increased chlorine retention after laundering is limited.

Under more drastic conditions of washing, similar to the AATCC 14-53 test method using a 10% soap solution (pH 9) at boil, the test fabric cured with magnesium chloride at 180° C. gave, in 5 repeated washes, a drop in crease recovery from 261° to 255°, decrease in $>NCH_2OH$ from 0.02% to 0.00% and an increase in chlorine retention from 0.049% to 0.087%. There was no significant loss in breaking strength after scorching of either the original or the washed samples. It thus appears that the main effect of mildly alkaline washing is to convert $>NCH_2OH$ to >NH, the change being faster at higher washing temperatures.

Role of Metal Salt Catalyst

The low chlorine damage obtained in the case of well-cured fabrics with metal salt catalysts is believed by Mosher [12] and others [9, 13] to be due to the buffering action of the oxides and carbonates of magnesium and zinc formed as an intrafiber de-

TABLE VI. Effect of Washing * on $>N\cdot CH_2OH$ Content and Chlorine Retention

Sample details		Free $>N\cdot CH_2OH$ %		% Chlorine retained		% Loss in breaking strength due to scorching	
		Original	Washed	Original	Washed	Original	Washed
$MgCl_2$	110° C.	0.449	0.197	0.173	0.372	80	87
$MgCl_2$	130° C.	0.276	0.164	0.118	0.246	59	74
$MgCl_2$	160° C.	0.110	0.084	0.061	0.101	1	0
$MgCl_2$	180° C.	0.083	0.066	0.049	0.073	0	2
$(NH_4)_2SO_4$	110° C.	0.345	0.173	0.167	0.305	73	77
$(NH_4)_2SO_4$	130° C.	0.240	0.131	0.132	0.213	66	73
$(NH_4)_2SO_4$	160° C.	0.164	0.110	0.108	0.153	53	55
$(NH_4)_2SO_4$	180° C.	0.141	0.122	0.104	0.132	49	50

* The samples were given ten washes at 50° C, in a 0.5% soap solution for 45 min. using an M : L ratio of 1 : 50.

TABLE VII. Effect of Hypochlorite Treatment on $>N\cdot CH_2OH$ Content

Sample details		pH of fabrics	Free $>N\cdot CH_2OH$, %		Free $>N\cdot CH_2OH$, %	
			Original	14 Hr. hypochlorite treatment	Alkaline hydrolyzed	Alkaline hydrolyzed and hypochlorite treated
$MgCl_2$	110° C.	7.9	0.410	0.282	0.000	0.060
$MgCl_2$	130° C.	8.2	0.293	0.223		
$MgCl_2$	160° C.	8.5	0.110	0.162		
$MgCl_2$	180° C.	8.5	0.083	0.131	0.000	0.074
$(NH_4)_2SO_4$	110° C.	7.9	0.368	0.263	0.013	0.065
$(NH_4)_2SO_4$	130° C.	7.8	0.240	0.192		
$(NH_4)_2SO_4$	160° C	7.9	0.185	0.174		
$(NH_4)_2SO_4$	180° C.	7.8	0.141	0.164	0.012	0.089

posit during curing. According to Mosher, the increase in chlorine damage obtained with these fabrics after repeated washing is due to the gradual removal, in washing, of these buffers from the fabric. On the other hand, Frick et al. [6] attribute the superiority of the metal salt catalysts to their high cross-linking efficiency. This is amply borne out by data on $>NCH_2OH$ given in Table II. A fabric sample treated with DMEU and magnesium chloride at 180° C. and given the usual process wash showed a magnesium content of 65 mg./100 g. fabric. After thorough washing with distilled water until the washings were free from magnesium, the fabric gave a magnesium content of 58 mg./100 g. fabric. The untreated fabric itself contained 38 mg. of magnesium per 100 g. fabric. Thus when magnesium chloride is used as a catalyst, some magnesium is retained by the fabric, probably as an intrafiber deposit of the oxide or carbonate as suggested by Mosher. This deposit, however, is very tenaciously held, and even after very thorough washing, a substantial proportion of it is retained. If one calculates magnesium required as oxide to neutralize the HCl equivalent to the chlorine retained by these fabrics (approximately 0.05% to 0.06%), the figure works out to approximately 18–20 mg. for 100 g. of the fabric. The magnesium content of the thoroughly washed sample and even of the untreated fabric is more than adequate to fulfill this requirement. On the other hand, chlorine retention of the treated fabric increased from 0.052 to 0.059 after thorough washing, and the strength loss due to scorching increased correspondingly from 0% to 7%. Increased chlorine retention after repeated washing has already been shown to be due to a gradual conversion of $>NCH_2OH$ to $>NH$.

With the ammonium salt catalysts, the chlorine damage is high but so is the content of chlorine rententive sites such as $>NCH_2OH$.

It thus appears that the superiority of the metal salt catalysts in reducing the chlorine damage of DMEU-treated fabrics is primarily due to their much greater cross-linking efficiency, leaving fewer sites in the finished fabric for chlorine retention.

Action of Hypochlorite

The standard AATCC Test 92-1958 for chlorine retention prescribes a treatment with 2.5 g./l. hypochlorite for 15 min. at 25° C., using a material to liquor ratio of 1:50. Presumably these conditions were selected to simulate conditions of domestic washing. In the short time of treatment with hypochlorite, the conversion of $>NCH_2OH$ and $>NH$ to $>NCl$ is by no means complete. Mention has been made earlier of an attempt to estimate the total chlorine retentive sites (that is, $>NCH_2OH$, $>NCH_2OCH_2N<$, and $>NH$ groups) in DMEU-treated fabrics by alkaline hydrolysis followed by treatment with hypochlorite, and determination of retained chlorine. For this estimation, hypochlorite treatment was continued until a constant value of retained chlorine was obtained. In a study of the effect of duration of hypochlorite treatment on the amount of chlorine retained by DMEU-treated fabrics, it was found that chlorine retention steadily increased and reached reasonably constant values after 10 to 12 hr. of treatment. A 14-hr. treatment with hypochlorite was therefore selected arbitrarily

for convenience of overnight working, and the eight samples of DMEU-treated fabrics were given this treatment. A determination of the $>NCH_2OH$ content of the fabrics after this treatment gave unexpected results (Table VII). The reduction in $>NCH_2OH$ was much less than expected after such a long treatment at pH 9.5. More puzzling was the fact that in three of the eight samples (magnesium chloride catalyst, cured at 160° and 180° C.; ammonium sulfate catalyst, cured at 180° C.), the $>NCH_2OH$ content actually increased significantly. To verify this, four of the samples, cured at 110° and 180° C., respectively, with either catalyst, were first given an alkaline hydrolysis for 72 hr. to convert all $>NCH_2OH$ and $>NCH_2OCH_2N<$ into $>NH$. These samples were then given the 14-hr hypochlorite treatment and again tested for $>NCH_2OH$. In each of the four samples, a small but significant amount of $>NCH_2OH$ was detected.

During the prolonged treatment with hypochlorite at 9.5 pH, the reaction $>NCH_2OH \rightarrow >NH + CH_2O$ is expected to occur, its extent depending on the initial amount of $>NCH_2OH$ present in the fabric. The data given in Table VII would indicate that in addition to this, another reaction, producing new $>NCH_2OH$, is also taking place. This may be due to a hydrolysis of the cross-links, probably preceded by a rupture of the ring.[1] In the samples where the initial $>NCH_2OH$ content is very low, the increase in $>NCH_2OH$ due to such a hydrolysis outweighs the small decrease in $>NCH_2OH$ due to its conversion to $>NH$, giving a net increase in $>NCH_2OH$ content.

In reality the situation is far more complicated, involving a decomposition of the hypochlorite and a loss of nitrogen and crease recovery from the fabric. These aspects are being studied in detail and will be reported later.

Summary and Conclusions

The chemical reactions involved in the curing of DMEU-treated cotton fabrics and during storage and laundering of such fabrics have been studied in reference to the chlorine-retention properties of the finished fabric. Chlorine retention is due to the presence of $>NH$, $>NCH_2OH$, and $>NCH_2OCH_2N<$ groups in the finished fabric.

$>NH$ groups are formed during curing by a partial thermal decomposition of $>NCH_2OH$ groups or by reaction of the small amount of monomethylol ethylene urea generally present in commercial DMEU. $>NCH_2OH$ groups are present in the cured fabric due to the incomplete cross-linking between cellulose and DMEU, their amount depending on the catalyst used and on severity of curing. Thus with metal salt catalysts and at higher curing temperatures, the content of $>NCH_2OH$ is reduced. Methylene ether groups are formed when magnesium chloride is used as a catalyst at low curing temperatures. $>NCH_2OH$ and $>NCH_2OCH_2N<$ can be estimated together by alkaline hydrolysis of the treated fabric with 0.5 *N* NaOH at 35° C. for 72 hr. and determination of the formaldehyde evolved.

When DMEU-treated fabrics are stored in an unwashed condition with the catalyst residues still present, extensive hydrolysis of the cross-links occurs, resulting in increased $>NCH_2OH$, loss of nitrogen and crease recovery, and greatly increased chlorine retention. Even when such fabrics are stored after a mild alkaline wash (fabric pH 7.5–9), an increase in $>NCH_2OH$ and chlorine retention is observed, but without loss of crease recovery. The full consequences of this increased $>NCH_2OH$ content on chlorine retention are realized only after repeated alkaline washings. Under these conditions, even fabrics which were given a "hard" cure with magnesium chloride catalyst followed by a thorough afterwashing, showed after five months storage a very high chlorine damage. These results bring into question the chlorine resistance of DMEU-treated fabrics even under the optimum processing conditions.

During laundering of DMEU-treated fabrics under mild conditions, $>NCH_2OH$ groups are progressively changed to $>NH$, thus increasing the rate of chlorine uptake from hypochlorite baths. On the other hand, prolonged treatment with hypochlorite solutions hydrolyzes the cross-links, probably after a preceding rupture of the CEU ring. The effectiveness of metal salt catalysts in reducing chlorine retention is primarily due to their much superior cross-linking efficiency. The role of metal oxides

[1] The alternative possibility that cross-links may break from the cellulose end by oxidation of the primary hydroxyl at the 6 position was pointed out by the reviewer of this paper. Untreated and DMEU-treated cotton, reacted for 14 hr. with hypochlorite under conditions given earlier showed a carboxyl content of 3 to 4 meq. for 100 g. of cellulose or one —COOH for about 200 glucose residues. The probability that these few —COOH should be in those glucose residues involved in cross-linking at 6 position is very small.

and carbonates as buffers against chlorine damage appears to be secondary.

An estimate of the potential chlorine damage that a DMEU-treated fabric will develop on repeated laundering can be obtained by performing the standard chlorine retention test on the finished fabric after giving it an alkaline hydrolysis treatment as described here. For the DMEU–metal-salt systems an estimate of $>NCH_2OH$ in the test fabric gives a reasonably accurate assessment of potential chlorine damage.

Acknowledgment

The authors are grateful to the Council of Administration of this laboratory for permission to publish these results.

Literature Cited

1. Bacon, O. C., Smith, J. E., and Hughes, L. E., *Am. Dyestuff Reptr.* **47**, P259 (1958).
2. Borghetty, H. C., *Textile World* **108**, No. 4, 99 (1958).
3. Cooke, T. F., Roth, P. B., Salsbury, J. M., Switlyk, G., and van Loo, W. J., TEXTILE RESEARCH JOURNAL **27**, 150 (1957).
4. Enders, H. and Pusch, G., *Melliand Textilber.* **40**, 315 (1959).
5. Flaschka, H. A., "EDTA Titrations," London, Pergamon Press, 1959, p. 75.
6. Frick, J. G., Jr., Kottes, B. A., and Reid, J. D., TEXTILE RESEARCH JOURNAL **29**, 314 (1959).
7. Frick, J. G., Jr., Kottes, B. A., and Reid, J. D., *Am. Dyestuff Reptr.* **48**, No. 13, 23 (1959).
8. Hofmann, K., "Imidazole and its Derivatives, Part I," New York, Interscience Publishers Inc., 1953, p. 228.
9. Marsh, J. T., *Textile Mfr.* **86**, No. 1023, 113 (1960).
10. Mehta, P. C. and Mehta, R. D., TEXTILE RESEARCH JOURNAL **30**, 524 (1960).
11. Mehta, P. C. and Mody, J. R., TEXTILE RESEARCH JOURNAL **30**, 532 (1960).
12. Mosher, H. H., TEXTILE RESEARCH JOURNAL **29**, 88 (1959).
13. Nuessle, A. C., *Am. Dyestuff Reptr.* **47**, 465 (1958).
14. Petterson, R. C., TEXTILE RESEARCH JOURNAL **29**, 840 (1959).
15. Petterson, R. C. and Grzeskowiak, U., *J. Org. Chem.* **24**, 1414 (1959).
16. Reid, J. D., Reinhardt, R. M., and Kullman, R. M. H., TEXTILE RESEARCH JOURNAL **28**, 247 (1958).
17. Reid, J. D., Reinhardt, R. M., Kullman, R. M. H., and Arceneaux, R. L., *Am. Dyestuff Reptr.* **49**, 527 (1960).
18. Rumens, W., Goetz, N., and Zeidler, Z., *Am. Dyestuff Reptr.* **49**, No. 20, 48 (1960).
19. Smith, A. R., *Am. Dyestuff Reptr.* **48**, No. 8, 49 (1959).

Manuscript received March 27, 1961.

The Physical Properties of Wool Fibers at Various Regains

Part IV: Mechanical Changes Due to "Incorporated" Water

M. Feughelman and I. C. Watt

Division of Textile Physics, C.S.I.R.O. Wool Research Laboratories, Ryde, Sydney, Australia

Abstract

Watt and Kennett [11] have shown that water may be incorporated into the keratin structure by long exposure at relative humidities between 5% and 80%. This incorporated water is not removed on drying *in vacuo* and results in an increase of the "dry" weight of the wool fibers. Mechanical tests carried out on fibers containing incorporated water show an increased stiffness for relative humidities less than 60–70% over stiffness measured at the same humidities after the incorporated water had been removed by saturation in liquid water. It is proposed that the water which is incorporated into the keratin structure and produces the "dry" weight increase becomes immobilized at intermediate relative humidities by increased strength of bonding of the water directly with the keratin structure. Saturation in liquid water reduces the amount of association between any one molecule and the keratin structure. Drying rapidly from this state hence lowers the possibility of formation of strong, direct bonds between water and keratin.

Introduction

Watt and Kennett [11] have shown that wool fibers exposed to water vapor with a relative humidity greater than 5% and up to intermediate humidities (<80% RH) give a higher subsequent equilibrium weight on desorption *in vacuo* than do fibers desorbed *in vacuo* from saturation. Wool fibers exposed to humidities ~50% RH show a maximum increase of their equilibrium weight *in vacuo* on desorption. This increase of equilibrium weight *in vacuo*, due to exposure to intermediate relative humidities, decreases with increase of humidity beyond ~50% RH and is negligible for humidities greater than 80% RH. It appears that at intermediate relative humidities some water is incorporated into the structure in such a way that it is difficult to remove. Further, it was pointed out that those fibers treated to have a high "dry" weight are mechanically stiffer [11] for low relative humidities than the same fibers at the same relative humidity which have had the extra incorporated water removed by saturation in liquid water prior to conditioning to the required relative humidity.

In this paper a survey is made of the increased mechanical stiffness of the fibers over a range of relative humidities at 20° C. Also a number of measurements at three relative humidities were carried out at 40° C. to note the trend in the mechanical properties of these *extra* "dry" weight fibers with temperature increase.

Procedure and Results

Using the technique described elsewhere [11], Corriedale wool was exposed to water vapor at 35° C. and 50% RH for 15 days. This exposure resulted in an increase of "dry weight" of 2.0%. That is, about 2.0% moisture above that present when the wool is equilibrated in distilled water and then dried was incorporated with the keratin structure. These Corriedale fibers after exposure at 50% RH were placed in a desiccator over silica gel and kept dry until used in the mechanical tests.

The fibers were mechanically tested at room temperature (20° C.) at various relative humidity values between 5% and 70%. A fiber was mounted in a stress measuring apparatus as described elsewhere [5]. First dry air was blown over the fiber. Then the fiber was brought to regain equilibrium at the

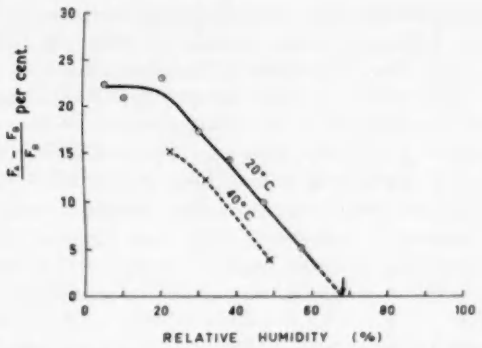


Fig. 1. The change of stiffness at 20° C. and 40° C. due to "incorporated" water in a wool fiber plotted against relative humidity. The change of stiffness is measured by the factor $(F_A - F_B)/F_B$. F_A and F_B are the forces acting on the fiber after 15 min. at 10% extension; F_A when the "incorporated" water is in the fiber and F_B when it is removed by wetting the fiber.

required RH by having air, conditioned to the required RH by passage over sulphuric acid solution at the appropriate concentration, blown over it for 1 hr. The fiber was then extended 10% in ½ min. and the stress relaxation recorded on the potentiometer for 15 min. After 15 min. the fiber was released from the strain and placed in distilled water at 52° C. for 1 hr. After this step the fiber was replaced in the apparatus, brought to the same RH using the procedure already mentioned. The stress relaxation was again recorded at 10% extension for 15 min. The force on the fiber at the end of 15 min. (a suitable arbitrary time) in the first experiment, F_A, was compared with the force, F_B, on the same fiber after 15 min. in the second experiment, i.e., after the fiber had been released at 52° C. in distilled water for 1 hr. This release treatment has been shown to return a fiber to its normal mechanical state [4].

The values of $(F_A - F_B)/F_B$ were measured at both 20° C. and 40° C. Figure 1 shows the results obtained at the different relative humidities for the two temperatures. Each point on the curve in Figure 1 represents the average of measurements on four to six fibers. At 20° C. measurements at 68% RH give no measurable difference between F_A and F_B.

Discussion

The increase of the force on a single fiber in the yield region for low relative humidities, when that fiber has had more water incorporated into its structure by lengthy exposure at ~50% RH, at first appears anomalous. More water normally increases the mobility of the keratin structure and weakens the bonding, in particular the hydrogen bonding, that is present. To consider the part played by this incorporated water it is necessary to consider first how the water is bonded into the keratin structure.

Aside from water chemically bonded in the keratin structure, water molecules [3] in the wool fiber would tend to associate by hydrogen bonding in the manner shown in Figure 2. The atoms at A and D would be oxygens, and at B and C hydrogens. However, these atoms, A, B, C, and D, can be either components of the keratin or of other water molecules. Coulson [3] points out that the hydrogen bonds formed, such as O—H····A, have a fairly strong directional force. This means that unless circumstances are favorable, a large proportion of water molecules, due to hindrances of the keratin–water structure, could exist in a state in which one or more of the hydrogen bonds indicated in Figure 2 is greatly weakened or even nonexistent.

Experiments on the keratin–water structure using nuclear magnetic resonance techniques, indicate an increase of mobility of the proton, and hence of the water molecules, with increase of relative humidity [12] (see Figure 3). This progressive increase

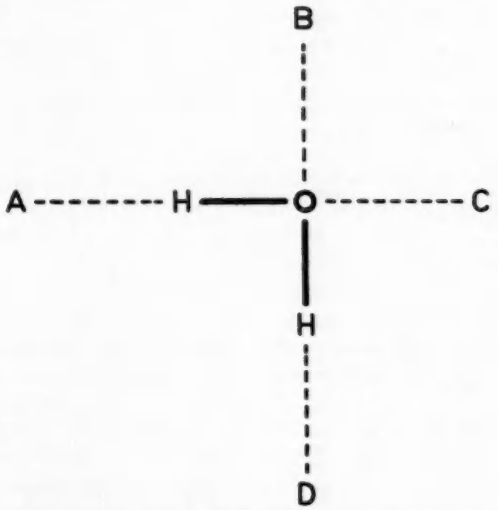


Fig. 2. The hydrogen bond associations possible for a water molecule in the keratin–water system. A and D are oxygen atoms and B and C hydrogen atoms.

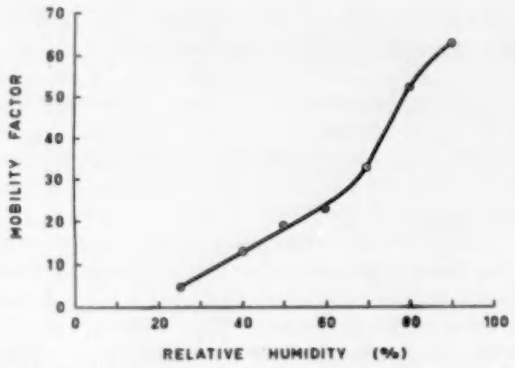


Fig. 3. The mobility factor obtained by nuclear magnetic resonance measurements for the water protons in the keratin–water system at various relative humidities.

indicates that the mobility of the water molecule tends to increase when there is an increase in the number of A, B, C, and D atoms which themselves are components of water molecules. The inverse of this would be that a water molecule is most firmly bound when all the A, B, C, and D atoms belong not to water molecules but to the keratin structure itself. Further, this immobility would increase with the correct alignment of the hydrogen bonds for maximum energy of bonding.

In interval sorption of water into the keratin–water structure the initial uptake of water is followed by a distinct, slower, second-stage absorption for the range of relative humidities from 5% to 80% [9, 10]. This second stage of sorption occurs over a period of hours or even days, and the keratin–water system may be considered in continuous equilibrium with the vapor pressure around the fiber. It has already been proposed that the second stage of sorption is produced by the mechanical relaxation of the keratin–water structure reducing the mechanical constraint on swelling and allowing for further moisture uptake. Further, water present in the fiber, as it became more tightly bound into the structure, would also show a drop in its vapor pressure. This means that further water sorption would take place to maintain equilibrium with the atmosphere around the fiber. A similar mechanism leading to increase in the binding of water in the keratin–water structure with time during interval sorption has been suggested recently, based on electrical conductivity experiments carried out in conjunction with those on water sorption [2]. From the above it appears that second-stage moisture sorption is a function of the keratin–water structure's ability to relax mechanically and possibly also change the bonding of its water. The proportion of second-stage moisture sorption has a maximum at about 50% RH. Above approximately 80% RH Watt observed no second-stage sorption (see Figure 4). As mentioned earlier, wool fibers exposed to humidities of about 50% RH show a maximum increase of their equilibrium weight *in vacuo* on desorption. Watt and Kennett [11] have shown also that changes in the "dry" weight for exposures to relative humidity above 80% are small. The inference may be drawn that the maximum incorporation of the water into the water–keratin structure requires conditions similar to those at the maximum proportion of second-stage water in interval sorption.

Further, the immobilization of water molecules can be shown to imply an increased mechanical stiffness of the associated keratin–water structure. The mechanical properties, such as stress relaxation of the wool fiber at a fixed strain, are dependent on the water associated with the keratin structure [7]. The keratin structure is made mobile by the water molecules having some mobility which are attached to it in the same way that large molecules are diffused in a solvent of small molecules by the movement of the small molecules [6]. The movement of a water molecule creates a vacant space into which the keratin chain may move. This movement of the chain would result in a stress redistribution. Fur-

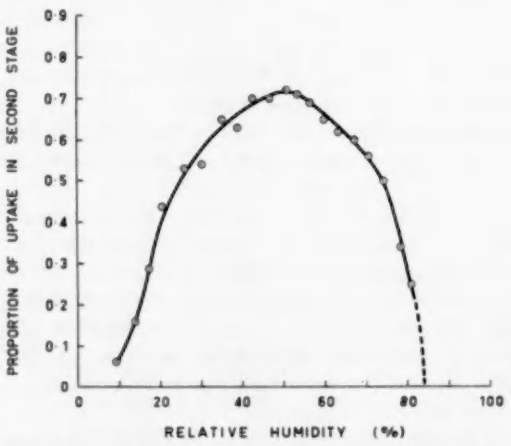


Fig. 4. Following a small relative humidity step change (interval sorption) let the total water taken up be Q_1 and the water taken up in the second stage of sorption Q_2. The figure shows Q_2/Q_1 plotted against the relative humidity.

ther, if water molecules in the structure are associated with other water molecules, a continuous network of hydrogen bonds (whether localized or almost continuous throughout the fiber) would be formed [1]. In a continuous network of hydrogen bonds under stress a redistribution of bonding by a "break–make" mechanism could occur to reduce the magnitude of the stress, i.e., the energy stored in the bonds under strain (see Figure 5), and so permit movement of the keratin structure. This type of redistribution of bonds would involve only the rupture of one hydrogen bond at a time.

Summarizing, the position is as follows:

1. If the water is mobile, it reduces the mechanical stiffness of the wool fiber by (a) assisting movement of the keratin structure; and (b) assisting in the redistribution of the stresses in the fiber in any hydrogen bond networks formed. This redistribution would both facilitate keratin structure movement and reduce the stress in the hydrogen bond network.

2. If the water is immobile it may assist in the mechanical strengthening of the fiber by forming stable hydrogen bonds, and thus stable cross-links, in the keratin–water structure. Also, the water may form a hydrogen bond cross-link, where, in the absence of water, due to the distance separating the two active sites, no linkage was possible. Such a mechanical reinforcing linkage due to water has already been postulated for the keratin–water system under different circumstances [8].

At 20° C. the increase in the mechanical stiffness of wool fibers at the fixed relative humidity due to incorporated water appears to be approximately constant from 5% RH to 20% RH (see Figure 1). No mechanical tests were carried out below 5% RH due to the difficulty of extending the fiber without breaking it. According to the picture presented so far, this result means that the water absorbed between 5% and 20% RH does not associate with the incorporated water to increase its mobility. Between 20% RH and about 60–70% RH the water which has entered the fiber at any fixed RH (progressively with increase of RH) increases the mean mobility of the incorporated water. This reduces the value of $(F_A - F_B)/F_B$, the mechanical stiffness increase due to the incorporated water. This again, interpreted, means that between 20% RH and 60–70% RH, water association with the incorporated water progressively increases. Above 70% RH the incorporated water has increased its association with other water molecules and so increased its mobility to such an extent that the value of $(F_A - F_B)/F_B$ has fallen to zero. The incorporated water at this stage is, as measured by its mechanical action, going from category 2 to category 1. It is of interest to note that results obtained from nuclear resonance measurements [12] indicate a rapid rise in the mobility of the water present in wool fibers above 70% RH. The effect of an increase of temperature would be to increase the mean mobility of the incorporated water. The drop in the value of $(F_A - F_B)/F_B$ for the same RH, when the temperature is increased from 20° to 40° C. (see Figure 1), indicates the increased mobility of the incorporated water and its reduced ability to increase the stiffness of the wool fiber.

Concluding Remarks

Water in excess of that present when a fiber is dried to 0% RH after equilibration in water (100% RH) is incorporated in the keratin structure when the fiber is dried after equilibration at lower relative humidities. The formation of this incorporated water is shown to be at a maximum after drying from about 50% RH. From the discussion of the state of water in the keratin–water structure developed in this paper, it appears that at 50% relative humidity, we have the optimum situation of water being mainly associated with the keratin structure and at the same time there being sufficient mobility of the water and the structure to allow the formation of optimum bonding of the water molecules into the structure. When the fiber is equilibrated at 100% RH most of the water present has only minor association with the keratin structure. On drying, far less rearrangement of the keratin–water structure can occur to create the conditions of optimum bonding, since such rearrangements must occur during the relatively

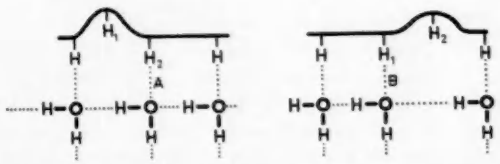


Fig. 5. A diagrammatic representation of a possible bond interchange between the keratin and water molecules, which form a network with the keratin (dark line). The heavy line represents the keratin structure. If bond A is under stress and the rupture of this bond and reformation of bond B reduces this stress, the hydrogen bond interchange will occur as indicated. This type of interchange may also aid in the movement of the keratin chains.

short drying period. This in turn means a greater ease of removal of the water on drying. The formation of strong associations between water molecules and the keratin structure is reflected in the mechanical changes produced on the wool fiber by these associations.

Literature Cited

1. Algie, J. E., Downes, J., and Mackay, B. H., TEXTILE RESEARCH JOURNAL **30**, 432 (1960).
2. Algie, J. E. and Watt, I. C., in preparation.
3. Coulson, C. A., *Research (London)* **10**, 149 (1957).
4. Feughelman, M., *J. Textile Inst.* **45**, T630 (1954).
5. Feughelman, M., TEXTILE RESEARCH JOURNAL **29**, 967 (1959).
6. Glasstone, S., Laidler, K. J., and Eyring, H., "The Theory of Rate Processes," New York, McGraw-Hill Book Co., Inc., 1941.
7. Haly, A. R. and Swanepoel, O. A., TEXTILE RESEARCH JOURNAL **31**, 966 (1961) (this issue).
8. Haly, A. R. and Feughelman, M., *J. Textile Inst.* **51**, T573 (1960).
9. Watt, I. C., TEXTILE RESEARCH JOURNAL **30**, 443 (1960).
10. Watt, I. C., TEXTILE RESEARCH JOURNAL **30**, 644 (1960).
11. Watt, I. C. and Kennett, R. H., TEXTILE RESEARCH JOURNAL **30**, 489 (1960).
12. West, G., Haly, A. R., and Feughelman, M., TEXTILE RESEARCH JOURNAL **31**, 899–904 (1961).

Manuscript received April 24, 1961.

Part V: The Nature of Birefringence

A. R. Haly

Division of Textile Physics, C.S.I.R.O. Wool Research Laboratories, Ryde, Sydney, Australia

O. A. Swanepoel

South African Wool Textile Research Institute, Grahamstown, South Africa

Abstract

The birefringence of Corriedale wool fibers was measured at nine different relative humidities. After being corrected for swelling the curve of birefringence against moisture content showed a minimum at a moisture content of 19% of the dry weight of the wool. At this point the birefringence is probably completely intrinsic, but at other moisture contents there may be a component of environmental birefringence. The curve shape may also be due in part to change of intrinsic birefringence with change of moisture content. Environmental birefringence is not likely to constitute more than approximately 9% of the total birefringence at any moisture content.

Introduction

Fraser [4] measured the birefringence of human hairs at various extensions and assumed that the birefringence was intrinsic, i.e., a function of the anisotropic polarizability of electron orbits, and not dependent on any particular morphological structure. Barnes [1] had previously measured refractive indices and birefringence of various wools both dry and at saturation regain, but did not determine the nature of the birefringence. Birefringence may arise when micelles or crystallites of one refractive index are immersed in a material of another refractive index. Neither of the substances need exhibit any intrinsic birefringence. Birefringence which arises in this way has been variously called form, textural, and environmental birefringence. The last term will be used here.

In recent years a level of structure in keratin has been revealed by electron microscopy which suggests the possibility of a large component of environmental birefringence. It has been shown that within a cortical cell there are a number of microfibrils embedded in a matrix. The microfibrils are aligned in the axial direction, and it is thought that they have a substantially more ordered structure than the matrix, and possibly a different chemical

constitution. Hence their refractive index may be different from that of the matrix. The microfibrillar diameter is about 80 Å, and their center-to-center distance is about 100 Å. Thus a model emerges which is similar to the classical one for rodlet, environmental birefringence.

In this paper we shall assume that any environmental birefringence which is found arises because of a difference in refractive index between microfibrils and matrix. It will be realized, however, that other structural units may be involved.

The usual imbibition methods for investigating environmental birefringence [5] rely on the assumptions that imbibed media of different refractive indices are not absorbed by the rodlets, and that the refractive index of the matrial surrounding the rodlets is that of the imbibed medium in its free state. The second assumption could not be entertained in the case of wool, where the microfibrils would be surrounded by a mixture (of unknown refractive index) of matrix and imbibed medium. Furthermore, it is very doubtful whether many liquids could be found which penetrate but do not cause some irreversible modification of the keratin.

From this point of view the most satisfactory liquid is water. It is thought that if water penetrates microfibrils at all, it is in relatively very small quantities [2]. By measuring birefringence of wool fibers at different water contents we may hope to gain some information about the nature of the birefringence even though the refractive index of hydrated matrix is not known.

This paper reports the results of such a series of measurements.

Experimental

All measurements were made on wool fibers from a Corriedale sheep.

The fibers were mounted in a stage extensometer, previously described [7], which permitted fiber rotation and observation under the polarizing microscope. The same specific positions on the fibers were used for measurement throughout the relative humidity range. If any rotation appeared following change of moisture content in a fiber, this was corrected before each measurement of birefringence.

Illumination was from a sodium lamp, and the distance travelled by the light through a fiber was measured only for ~0% RH. At other values of relative humidity the distance was calculated, using the diametral-swelling data published by the Wool Industries Research Association [15]. The values of dry diameter may be in error by about 5%, so that our determination of absolute value of birefringence at a single point may be in error by a slightly larger amount. Our primary interest, however, is in changes of birefringence.

TABLE I

RH, %	Wt. glycerol/wt. solution
0	100
25	92
40	84
50	78.5
60	72.3
70	64
80	52
90	35
100	0

To obtain required relative humidities around the fibers they were immersed in aqueous glycerol solutions of concentrations shown in Table I.

The glycerol concentration vs. relative humidity data were taken from the work of Hermans [10]. It was thought that some glycerol might penetrate the fibers at the higher relative humidities, but measurements of birefringence showed no change over periods of time much greater than were required for a measurement.

To condition a fiber to the required relative humidity it was first rinsed with some of the glycerol solution, and then immersed in another aliquot of the same solution. Thereafter, a minimum time of 15 min. was allowed for the moisture content to approach equilibrium. Checks were made to ensure that longer times produced no further change. Results were obtained when the desired regains were approached by both absorption and desorption. The sequence in which the regains were taken was changed without effect on the measured values of birefringence.

Measurements of birefringence were made using the method employed by Barnes [1]. The technique was also described by Goranson and Adams [6]. The method yields a phase-angle $\theta/2$, and the birefringence is then given by

$$n_{\parallel} - n_{\perp} = (\theta \times 5890)/(360 \times d)$$

where θ is measured in degrees, d is the distance travelled by the light through the fiber, and 5890 Å

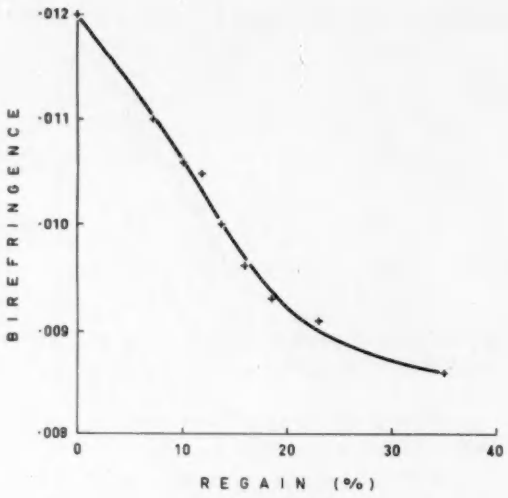


Fig. 1. Measured values of birefringence of wool fibers plotted against regain.

is taken as the wavelength emitted by the sodium lamp. Repeat measurements showed that the error in measurement of θ was about 1%.

The measurements were made at room temperature, which was in the vicinity of 25° C.

Results

At each relative humidity the birefringence was measured at the same twelve specific positions on three fibers. Thus each point on the graphs is the mean value from twelve readings. In Figure 1 the mean birefringence, calculated using the above equation, is plotted against moisture content of the fibers. The moisture content (regain) is expressed as a percentage of the dry weight of the wool, all such values being obtained from the isotherm of Speakman and Cooper [14] and the known relative humidities. Every set of measurements taken at a particular point gave a curve similar to that of Figure 1, but with a greater scatter about the mean line. It appeared, in agreement with Barnes's [1] results, that true birefringence values may change from fiber to fiber.

Figure 1 shows that the birefringence of Corriedale wool increases from 0.0086 in the wet state to 0.0120 when dry, i.e., a rise of 39.5%. This is in good agreement with Barnes's results for Leicester and Cotswold wools, the corresponding figures for these being 41.5% and 38%. Before we can make any deductions about the effect of moisture content on birefringence it is necessary to correct the data of Figure 1 for the effect of dilution. As the swelling increases there is a corresponding decrease in the number of birefringent elements in any unit volume of the fiber. The corrected value if the birefringence is intrinsic is given by

$$(n_{\parallel} - n_{\perp})_c = (n_{\parallel} - n_{\perp})v_s/v_d$$

where $(n_{\parallel} - n_{\perp})$ = measured value of birefringence, $(n_{\parallel} - n_{\perp})_c$ = corrected value, v_s = volume of fiber in the swollen state, and v_d = volume of dry fiber.

Birefringence values corrected in this manner, with the aid of volume swelling data published by the Wool Industries Research Association [15], are shown in Figure 2. It will be seen that $(n_{\parallel} - n_{\perp})_c$ falls to a minimum at a moisture content in the vicinity of 19%.

Discussion

When a material which gives only environmental birefringence is saturated successively by penetrants of increasing refractive index, n, the graph of birefringence against n shows a minimum at the value of n which is the same as the refractive index of the rodlets or micelles. Furthermore, the graph is approximately symmetrical about an imagined axis of symmetry [5]. An example of this type of relationship may be seen in Figure 5, curve B. If a material shows both intrinsic and environmental

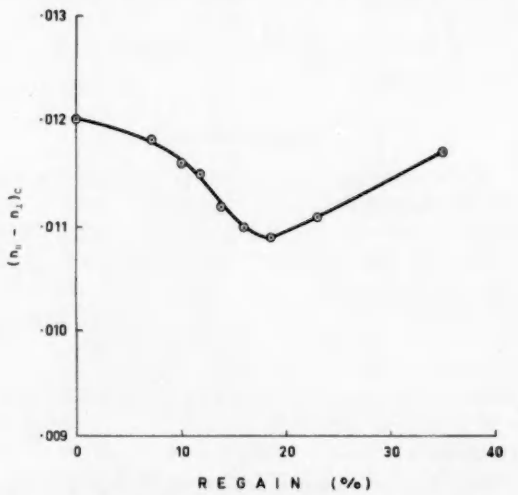


Fig. 2. Measured values of birefringence after correction for swelling, plotted against regain.

birefringence the rodlets or micelles will exhibit at least two refractive indices and it will not be possible to obtain a precise refractive index match. In this case the graph will show a minimum at a value of n which is the mean of $n_{\parallel}$ and $n_{\perp}$ for the rodlets. At this minimum, to a good approximation, any residual birefringence is intrinsic.

If the graph in Figure 2 had been a straight line parallel to the regain axis the conclusion would have been that the rodlets possessed a constant intrinsic birefringence at all regains and that there was no environmental birefringence. In fact the figure indicates that at 19% regain the birefringence is intrinsic and that at other regains either the intrinsic birefringence is greater or some environmental birefringence is present. The data show that environmental birefringence will not exceed approximately 9% of the total birefringence at any moisture content. We shall attempt to calculate the possible magnitude of a component of environmental birefringence.

Environmental Birefringence

It appears possible that the refractive index of the matrix–water complex changes with moisture content in such a way as to yield, from the data of Figure 2, the curve shape associated with environmental birefringence. It is necessary to assume that in the dry fiber the refractive index of the matrix is greater than that of the microfibrils. This follows because addition of water must reduce the refractive index of the matrix, bringing it to equivalence with that of the microfibrils at 19% regain. Though it is not common for a crystalline material to have a lower value of n than an amorphous material of similar composition, such cases are known, e.g., ice and water. In addition, the density of crystalline keratin as calculated from models such as the coiled-coil of Pauling and Corey [13] is less than the measured density of wool [3].

In attempting to find whether the curve shape of Figure 2 can be explained in terms of environmental birefringence, the method followed will be to calculate, using some simplifying assumptions, the refractive index of the matrix–water complex. Hence we shall obtain the curve showing the relationship between environmental bifringence and regain. The assumptions used are:

1. All swelling due to water absorption takes place in the matrix.

2. In the dry fiber the mass and volume of matrix are the same as the mass and volume of the microfibrils.

3. The refractive index of the matrix–water complex is the same as the mean refractive index of microfibrils at the regain corresponding to the minimum in the curve of Figure 2.

4. It is valid to use (following Hermans [11]) the Gladstone and Dale relationship between refractive index and density.

Assumptions 1 and 2 should be sufficiently accurate to give a first approximation to the relationship between birefringence and regain. No judgment can be made about the validity of 3. The work of Hermans [11] encourages the belief that 4 is a reasonable assumption.

Proceeding, we have from Hermans' work

$$V_a(n_a - 1) = V_0(n_0 - 1) + 0.333a \qquad (1)$$

where in our case V_0 = volume of 1 g. of dry matrix; n_0 = refractive index of dry matrix; V_a = volume of swollen matrix; n_a = refractive index of swollen matrix; and a = moisture content of swollen matrix expressed as grams of water per gram of dry matrix. If s is the volume swelling of the whole fiber and R is the moisture content of the whole fiber the equation becomes

$$V_0(1 + 2s)(n_a - 1) = V_0(n_0 - 1) + 0.666R \qquad (2)$$

Taking $\bar{V}_0 = 0.767$ [15] and $\bar{n}_0 = 1.55$ and using the same regain and swelling data as before [15] we calculate n_a. The resulting plot of n_a against regain is shown in Figure 3. At 19% regain $n_a \sim 1.52$, and this value is now used as the con-

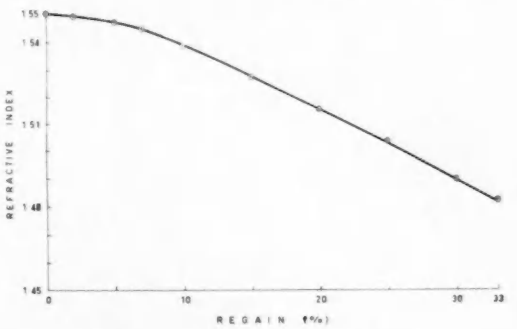


Fig. 3. Calculated refractive index of matrix plus water complex plotted against regain of the whole fiber. (For assumptions made in calculation see text.)

stant refractive index of microfibrils in Wiener's equation for rodlet environmental birefringence. The equation is (see for instance, Frey-Wyssling [5])

$$n_{11}^2 - n_\perp^2 = \frac{v_1 v_2 (n_1^2 - n_2^2)^2}{(v_1 + 1)n_2^2 + v_2 n_1^2}$$

where v_1 = volume fraction of rodlets; v_2 = volume fraction of surrounding medium; n_1 = refractive index of rodlets; and n_2 = refractive index of surrounding medium. We note that to a first approximation $(n_{11} + n_\perp)$ and $(n_1 + n_2)$ are constant, so that we may use the equation

$$n_{11} - n_\perp = \frac{K v_1 v_2 (n_1 - n_2)^2}{(v_1 + 1)n_2^2 + v_2 n_1^2}$$

where K is approximately equal to 3.1.

The values of $n_{11} - n_\perp$ obtained from this equation were multiplied by V_s/V_d to make the resulting graph comparable with Figure 2. The results are shown in Figure 4. As in Figure 2 a point of inflection is present at low regain, but the curve is much more symmetrical than the experimental curve.

In Figure 5, curve B, the same calculated and corrected environmental birefringence data are plotted against calculated refractive index of the matrix–water complex. Curve A of the same figure is the graph of measured and corrected birefringence against calculated refractive index of the matrix. (Note that the ordinate scales are different for the two curves.) In curve A a point of inflection remains at low regain (refractive index of about 1.54), which is absent in curve B. To the left of the minimum, the largest environmental birefringence indicated by curve B is only one-third of the corresponding change in curve A. To the right of the minimum the greatest change in B is one-eighth of the corresponding change in A. Even though the amount of calculated environmental birefringence is dependent on the uncertain quantity $(n_1 - n_2)$ it seems unlikely that all the change in birefringence on both sides of the minimum in curve A is to be explained on the above theory. However, in view of the general shape of the graph of Figure 4, it may be unwise to exclude the possibility that a more sophisticated analysis on the same lines would be consistent with the data.

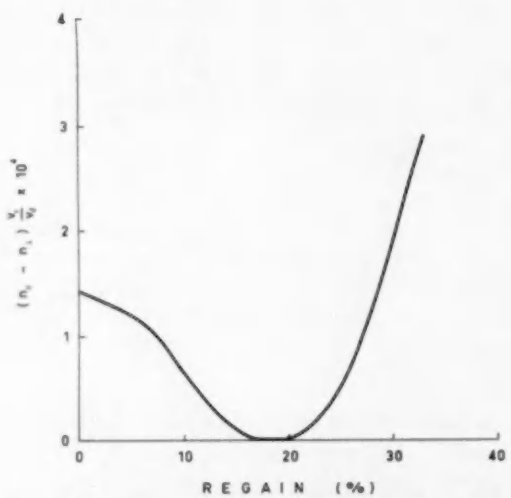


Fig. 4. Calculated environmental birefringence V_s/V_d plotted against regain of the whole fiber.

Possible Changes in Intrinsic Birefringence

The changes on either side of 19% regain may be partially produced by at least two other mechanisms.

1. At dryness a fiber may have internal strains which are responsible for a component of birefringence. A wool fiber forms and hardens under conditions far removed from the dry state and it is possible that drying produces, for instance, compression of the microfibrils and positive strain in the matrix. It is difficult to predict the net effect of these deformations on fiber birefringence but such a process appears capable, in principle, of explaining at least some of the fall in $(n_{11} - n_\perp)_c$, Figure 2, between dryness and 19% regain. Hermans [11] discussed a similar situation in the case of cellulose. If at 19% regain the fibers were free of internal strains, then at higher regains strains may again be present and be responsible for some of the increase in birefringence above 19% regain.

If the microfibrils are progressively compressed as equilibrium regain falls below 19%, we have a ready explanation for the longitudinal swelling of wool at different moisture contents. At 19% regain about 95% of the total length swelling has taken place, the subsequent change to saturation regain, ~33%, producing little change in fiber length.

2. It is known that a sufficiently concentrated solution of LiBr at room temperature virtually destroys the birefringence of wool [8]. On removal of the LiBr, birefringence is restored. The birefringence is progressively destroyed as the

penetrating front of reagent travels from fiber cuticle to fiber axis; i.e., it is lost prior to supercontraction and accompanying large-scale disorientation of molecular chains. The possibility arises that the presence of absorbed water disturbs the electron orbits in the keratin sufficiently to produce a much smaller, reversible loss of intrinsic birefringence. This mechanism could explain some of the fall in $(n_{\parallel} - n_{\perp})_c$ between 0% and 19% regain. Above 19% regain it is thought that much of the added water condenses onto previously absorbed water molecules, so that the effect may be small in this regain region. It is interesting to note that Barnes [1] found that when wool fibers were immersed in methanol their birefringence fell to a value 8% lower than the value in water. He found a smaller fall when ethanol was used and an increase when propanol was used. In the latter two cases, it is probable that insufficient time was allowed for the penetrants to reach equilibrium with the wool. The present authors found that ethanol caused the birefringence to fall 15.5% below the value in water. Thus it appears that each of the reagents, H_2O, CH_3OH, and C_2H_5OH, in that order, reduce birefringence to a lower value. This effect cannot be ascribed solely to the different refractive indices of the media since methanol has a lower index (1.331) than either water (1.333) or ethanol (1.362). Neither is there a direct correlation with dipole moment, methanol again having the lowest value (1.68 debye units). For ethanol the value is 1.70 and for water 1.87 debye units. The values of dipole moment were measured in the gas phase in all cases and were obtained from the table published by Le Fèvre [12].

In speculating about what may be the basic structural unit yielding intrinsic birefringence we note Fraser's [4] calculated value (0.012) for birefringence of the α-helix. This is in good agreement with the present measured value of intrinsic birefringence. However, as Fraser remarked, not too much weight should be placed on the calculated value. We have mentioned that aqueous LiBr above a fairly critical concentration destroys birefringence before much disorientation of the molecular chains is permitted. In addition Haly and Snaith [9] found that both birefringence and the α-helical structure of wool were destroyed by aqueous LiBr over the same small concentration range. It is probable that this reagent breaks the intrahelical hydrogen bond between the peptide

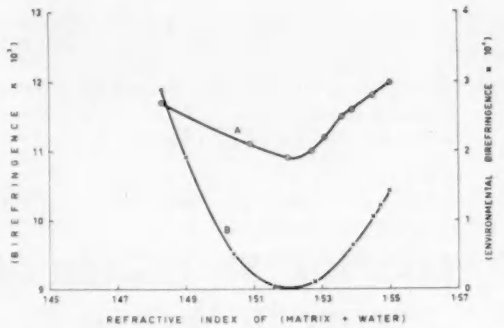


Fig. 5. Curve A: Corrected measured birefringence (ordinates at left) plotted against calculated refractive index of matrix plus water. Curve B: Calculated environmental birefringence $x(V_s/V_d)$ (ordinates at right) plotted against calculated refractive index of matrix plus water.

—NH and —CO groups, thus allowing sufficient disordering to cause the α-pattern to vanish. Since intrinsic birefringence does not require the presence of crystallites but merely of aligned molecules it should be less critically dependent on small disturbances than the α-pattern seen by X-ray diffraction methods. The fact that it vanishes under the same circumstances as does the α-pattern may mean that a large fraction of the birefringence is due to the bonds participating in the intrahelical —NH···O=C— complex, so that rupture of the hydrogen bond allows a large decrease in anisotropic polarizability, and hence loss of birefringence.

Literature Cited

1. Barnes, R. J., Ph.D. thesis, Leeds University (1933).
2. Fraser, R. D. B., MacRae, T. P., and Rogers, G. E., *Nature* **183**, 592 (1959).
3. Fraser, R. D. B. and MacRae, T. P., TEXTILE RESEARCH JOURNAL **27**, 384 (1957).
4. Fraser, R. D. B., *Nature*, **172**, 675 (1953).
5. Frey-Wyssling, A., "Submicroscopic Morphology of Protoplasm and its Derivations," Amsterdam, Elsevier Publishing Co., 1948, pp. 57–67.
6. Geranson, R. W. and Adams, L. H., *J. Franklin Inst.* **216**, 475 (1933).
7. Haly, A. R. and Feughelman, M., *J. Textile Inst.* **51**, T573 (1960).
8. Haly, A. R. and Griffith, June, TEXTILE RESEARCH JOURNAL **28**, 32 (1958).
9. Haly, A. R. and Snaith, J. W., *Biochim. et Biophys. Acta* **44**, 180 (1960).
10. Hermans, P. H., "Contribution to the Physics of Cellulose Fibres," Amsterdam, Elsevier Publishing Co., 1946, p. 27.

11. Hermans, P. H., "Contribution to the Physics of Cellulose Fibres," Amstrdam, Elsevier Publishing Co., 1946, pp. 109–129.
12. LeFèvre, R. J. W., "Dipole Moments," London, Methuen and Co., 1948.
13. Pauling, L. and Corey, R. B., *Nature* **171**, 59 (1953).
14. Speakman, J. B. and Cooper, C. A., *J. Textile Inst.* **27**, T183 (1936).
15. Wool Industries Research Association, "Wool Research," Vol. 2, Leeds, 1955, p. 13.

Manuscript received May 16, 1961.

Relaxation Shrinkage of Wool Fabrics: Its Occurrence in Worsteds and Dependence upon Cloth Structure

K. Baird

Division of Textile Physics, C.S.I.R.O. Wool Research Laboratories, Ryde, Sydney, Australia

Abstract

Relaxation shrinkage measurements have been made on seven worsted fabric structures from five different mills. It appears that the warp shrinkages differ significantly between mills and also between structures; by contrast no regular variation was discerned for the weft shrinkages.

Examination of the load–extension curves of these fabrics has shown big differences in the extensions which occur in the warp direction at loads typical of those found in finishing machines. A linear relationship between relaxation shrinkage and fabric extensibility in the warp direction is shown to hold for all mills.

Introduction

A brief review of the published work on relaxation shrinkage has recently been given elsewhere [1]; many aspects of the subject have been studied by a number of workers, but the possible effect of weave structure seems to have been omitted so far. Different weaves have been utilized in different sets of experiments, but any relationship between shrinkage and structure has been masked by other factors.

It is common knowledge in the woolen and worsted industries that some types of fabric are more difficult to finish free of relaxation shrinkage than others. Such troubles occur in cloths which feel "springy" when tensioned lightly, this "springiness" being a consequence of the cloth construction. Where the weave crimp in a fabric is large, the structure as a whole can extend readily even under low tension. Cryer [2] takes note of this effect of construction on shrinkage when he states, "Experience may indicate . . . that fabrics in which the yarns bend a great deal . . . are likely to be troublesome [to the tailor, because of relaxation shrinkage]." Thus it seems that a quantitative explanation of how structure affects relaxation shrinkage would clarify an important aspect of the subject.

The present work is intended as a fairly restricted survey of the relaxation shrinkages in worsted fabrics from some Australian mills. The load–extension curves of a number of fabric structures are examined, and a general relationship between fabric extensibility at a low load and relaxation shrinkage is shown. Considering the broad similarity in finishing machines and methods in various countries, it is expected that the results of the survey and the analysis will have a wide application.

Experimental

Seven worsted fabric structures, all 100% wool, were chosen as being representative of the range of worsteds produced by local mills. These were: plain, hopsac, serge, gabardine, pick and pick, venetian, and barathea. Each of five mills supplied two

sample lengths of each fabric in the finished state. Table I gives details of one typical fabric selected from each group. The wool qualities, yarn counts, loom settings, and finishing routines all varied from fabric to fabric and from mill to mill, since the sample lengths were drawn from their normal production ranges.

Relaxation shrinkages were measured by the following method. One sample, 30 cm. square, was cut from each length and marked with a 25 cm.-square grid of eight small spots, permitting three measurements of length to be made in both the warp and weft directions. After the samples had been conditioned at 65% RH, 20° C., the initial measurements and weights of each were noted. The samples were then immersed for 30 min. in a water bath, controlled at 50° C., which consisted of distilled water with 0.1% of non-ionic detergent added. The samples lay flat on open mesh trays and were not subjected to any agitation. They were removed without distortion and allowed to come to equilibrium regain at standard conditions. A second set of length measurements and weighings was then made. The differences between the initial and final dimensions were averaged over the three measurements in each direction, and expressed as percent change of the original.

It is important that the regains of the samples during the initial and final measurements should be the same to within 0.3%. This is necessary because of the occurrence of "hygral expansion" [1] or reversible change of dimensions with regain, which always occurs to some extent in wool fabrics. In some cases the hygral expansion can be 1% change in linear dimensions for a 3% change in regain. For this reason all samples were weighed at the time of measurement, and in those cases where a change of weight of 0.3% or more occurred, a suitable correction was made to the measured lengths. The correction was assessed from a separate set of data on the hygral expansion curve (dimensions vs. regain) which was determined for each fabric tested.

The load–extension curves were obtained for each sample using 20 cm. × 5 cm. strips cut in the warp direction from the 30-cm.-square samples which had been relaxed in the first part of the work. An Instron textile testing machine was used, the rate of extension being 50%/min., and the maximum load, 1 kg. All samples were conditioned at 65% RH, 20° C. before and during the tests. Values of load were converted to the equivalent load on a full width fabric (1.5 m.) and are quoted as such throughout the paper.

Analysis of Results

A. Table II displays the observed values of relaxation shrinkage for the 35 fabrics, each figure shown being the average of six measurements. The means

TABLE I. Details of Typical Fabrics Used

Weave	Weight, oz./lin. yd.	Width, in.	Warp yarns			Weft yarns			Threads/in. (finished)	
				Count			Count			
			Quality	Wstd.	Tex	Quality	Wstd.	Tex	Warp	Weft
Tropical 1/1 plain	11	58	64	2/34	2/26	64	2/34	2/26	49	44
Hopsac 2/2 plain	14	58	60	2/36	2/24.5	60	2/36	2/24.5	72	66
Serge 2/2 twill	14.5	58	60	2/36	2/24.5	60	2/36	2/24.5	77	63
Gabardine 2/2 twill	15	58	64	2/44	2/20	64	2/44	2/20	111	60
Pick and pick 2/2 twill	14.5	58	60/64	2/36	2/24.5	60/64	2/36	2/24.5	68	64
Venetian 5-thread warp face sateen	14	58	60	2/40	2/22	60	1/19	1/46.5	92	64
Barathea 5-thread sateen	14.5	58	64	2/44	2/20	64	1/26	1/34	87	83

TABLE II. % Relaxation Shrinkage of 35 100% Wool Worsted Fabrics

Mill	Weave: Plain Warp	Plain Weft	Hopsac Warp	Hopsac Weft	Serge Warp	Serge Weft	Gabardine Warp	Gabardine Weft	Pick & pick Warp	Pick & pick Weft	Venetian Warp	Venetian Weft	Barathea Warp	Barathea Weft	Mill averages Warp	Mill averages Weft
1	0.9	1.3	1.2	1.8	2.8	1.6	2.7	2.8	1.4	1.6	2.9	1.7	3.3	1.1	2.2	1.7
2	1.5	0.5	2.0	3.2	3.4	1.9	3.4	1.8	1.6	0.8	2.7	0.2	2.7	0.7	2.5	1.3
3	0.4	0.6	0.7	1.0	1.7	0.3	1.9	0.0	1.4	1.0	2.8	1.0	1.0	0.4	1.4	0.6
4	1.5	0.3	0.7	0.8	1.1	0.5	2.7	0.7	0.7	0.7	2.6	0.5	2.6	1.8	1.7	0.8
5	2.3	2.2	2.2	0.4	1.6	0.6	3.9	0.2	2.3	0.6	6.1	0.8	3.2	1.3	3.1	0.9
Weave averages	1.3	1.0	1.4	1.4	2.1	1.0	2.9	1.1	1.5	0.9	3.4	0.8	2.6	1.1	2.17	1.04

for each structure over all mills, and for each mill over all structures, are shown in the bottom row and the last column, respectively. An analysis of variance of these figures was made.

There was a significant difference (at the 2% probability level) between the grand mean warp shrinkage (2.17%) and the grand mean weft shrinkage (1.04%). Following the completion of this survey, the shrinkage figures for a further 21 fabrics, distributed evenly over the seven structures, have been added without changing the mean shrinkages appreciably. The mean warp and weft relaxation shrinkages for the 56 fabrics were 2.23% and 0.97%. This significant difference indicated some difference in the basic causes of shrinkage in the warp and weft directions, and separate analyses were carried out on the two sets of figures.

The analysis of the warp shrinkage figures showed that there were differences between the fabric structures, taken over all the mills, and also that there were differences between mills, taken over all fabrics. These differences were significant at the 1% probability level in both cases.

The analysis of the weft shrinkage figures revealed that there were no significant differences between mills, nor between fabrics, taken over all mills.

B. Load–extension curves for three fabrics of different structures are reproduced in Figure 1. They correspond to the three fabrics which are shown in cross section in Figure 2, and are a gabardine, a barathea, and a hopsac. The upper and lower curves were those which exhibited the greatest and the least extensibility of all the fabrics examined in the survey. As already mentioned, the abscissa of Figure 1 has been adjusted to represent the load on a full width (1.5 m.) of fabric, although the test was carried out using a strip 5 cm. wide. These curves illustrate the big differences in extensibilty which occur in different structures. The corresponding fabric cross sections of Figure 2 suggest that the greater the warp yarn crimp is in any structure, the more easily it may be extended, in spite of the restraining influence of the weft yarns; this is in fact found to be generally true.

In order to discover whether a relationship existed between the relaxation shrinkage in the warp direction and fabric construction, the load–extension curves of all fabrics of Table II were examined, and the extensions were noted at a load of 4.0 kg. on each. This load had been chosen as being representative of mill practice upon the basis of two sets of observations:

1. Two fabrics of known load–extension characteristics were followed through a complete finishing routine, and the extensions introduced in the warp direction by each machine were measured. Those extensions which resulted in relaxation shrinkage in

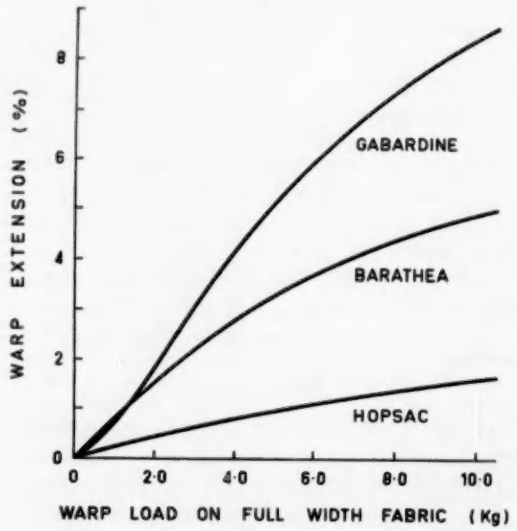


Fig. 1. Load-extension curves for three fabrics.

the finished fabric corresponded to fabric tensions over the full width, lying between 2.5 and 5.5 kg.

2. An accurate laboratory model of the tension rails on the mill machines was constructed, and the tensions on narrow strips of fabric running through the rails were measured. These measurements confirmed the figures given above.

After extracting from each curve the extension of the sample at 4.0 kg. load, the nature of the relationship between the relaxation shrinkage and the fabric extension was examined. This was done by means of a regression analysis, in which the relation $y = ax + b$ was estimated between the dependent variable y (relaxation shrinkage) and the independent variable x (extension at 4.0-kg. load). This was carried out for the seven fabrics from each mill, and these separate analyses showed values of the regression coefficient, a, which did not differ significantly (at better than the 1% probability level) between mills.

This showed that the shrinkage depended upon the fabric extension at 4.0-kg. load in a similar way in every mill; the existence of a general relationship between the variates was thus firmly established. The average values of extension and shrinkage for each structure have been taken over all mills, and the resulting relationship is shown in Figure 3 for the seven structures.

An analysis of covariance of the shrinkages was made to determine whether differences occurred between the regression coefficients, b, for the five mills. Differences, significant at the 1% level, were found. This result shows that the mean shrinkages from the mills were still different after they had been adjusted to a common fabric extensibility.

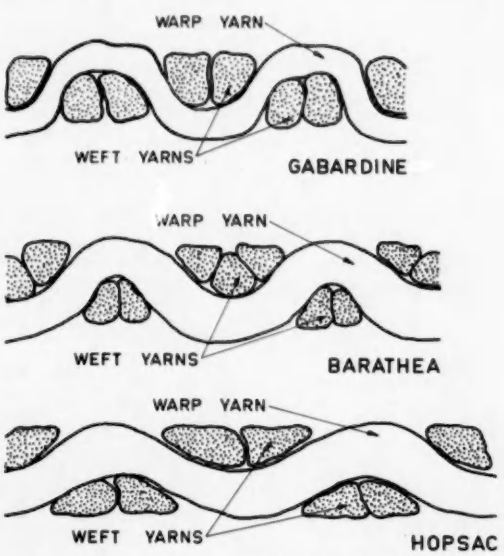


Fig. 2. Cross sections of three fabrics.

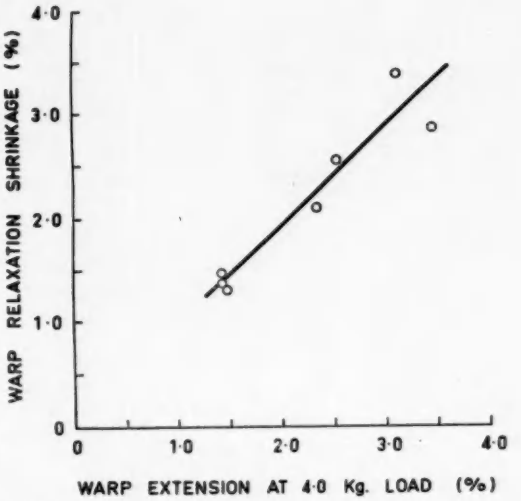


Fig. 3. The relationship between the average values of extension and shrinkage for seven fabric structures taken over all mills.

Discussion

The analysis given under A has shown quite clearly that some fabric structures are more likely to suffer from a large relaxation shrinkage in the warp direction than others; this is true of fabrics from all mills. The results of the analysis under B show why this is so.

Figure 3 represents a clear relationship between relaxation shrinkage and fabric extension at a low load, which holds for all mills included in the survey. This indicates that there is a general tendency within each mill to hold the tensions constant in the various finishing machines for all fabric structures; consequently those cloths which are more extensible are stretched more, and subsequently shrink more under conditions of steaming or wetting.

The shape of the load–extension curves for very extensible fabrics suggests that loads in the finishing machines should be kept to 2.0 kg. or less to avoid the stretching which results in troublesome shrinkage. It will be appreciated that this is a very low load when spread across the width (normally

1.5 m.) of fabric; the arrangements necessary to bring the load down to such low values and still maintain the effectiveness of the machines involved may be quite difficult to achieve. It has been observed that in many instances existing steaming or dewing machines do leave worsted fabrics almost free of relaxation shrinkage; so, provided the low tensions indicated can be used in subsequent machines, the incidence of troublesome relaxation shrinkage in finished fabrics should be very low.

Part A of the analysis also shows that some mills tend to produce fabrics of all types with consistently lower relaxation shrinkages than others do. Following the high degree of correlation which has been shown between shrinkage and fabric extensibility, two possible causes for this are suggested: (a) that there are significant differences in the average extensibilities of fabrics from the different mills, or (b) that differences exist, on the average, in the conditions during finishing, e.g., one mill using, in general, lower tensions in its machines than another.

It can be shown by a simple analysis that significant differences (a) do not exist. It seems likely that (b) is the real cause, and the second part of analysis B supports this. This analysis shows that when the effects of fabric extensibility are removed, significant differences still remain in the average shrinkage figures from the various mills. In view of the dependence of relaxation shrinkage upon the fabric extension under load, it seems clear that the conditions during finishing—and in particular the tensions which are applied—are of prime importance in causing the differences in relaxation shrinkage which occur between mills.

Conclusions

It seems to be generally true of worsted fabrics from Australian mills that relaxation shrinkage in the warp direction is greater than in the weft. Warp shrinkages vary significantly between fabrics of different structure types when averaged over a number of mills; also there is a significant variation between mills, when averaged over the range of structures considered.

Weft shrinkages appear to vary in a random way both within mills and within fabric types.

A correlation has been shown between the average load–extension behavior of different structures and their average warp shrinkages. This suggests that the main reason for the occurrence of the latter is the existence of tensions of about 4.0 kg. in the various finishing machines.

It has been demonstrated that the differences which occur between average mill shrinkages are not due to different average fabric extensibilities; it seems certain that differences in machine tensions during finishing are mainly responsible.

Acknowledgments

The author extends his warm appreciation to Mr. W. B. Hall of the Division of Mathematical Statistics for calculations and valuable discussions on the statistical analyses. He is also indebted to the firms who supplied the fabrics used in the study.

Literature Cited

1. Baird, K., TEXTILE RESEARCH JOURNAL **31**, 624–629 (1961).
2. Cryer, H., *J. Textile Inst.* **26**, P331 (1935).

Manuscript received April 24, 1961.

The Accelerotor as a Test Machine for Felting Shrinkage

G. L. Stott

Division of Textile Physics, C.S.I.R.O. Wool Research Laboratories, Ryde, Sydney, Australia

Abstract

Results of felting shrinkage tests on a number of worsted and woolen fabrics using a modified form of the AATCC Accelerotor [1] abrasion tester reveal a significant relationship to shrinkages obtained in three domestic washing machines. This, together with the rapidity with which these tests can be carried out, show that the modified Accelerotor could be useful as a laboratory-scale felting-shrinkage tester.

Introduction

There has long existed a need for a test of felting shrinkage which would not only be rapid in operation and suitable for laboratory use, but the results of which would bear some relation to results obtained from domestic laundry machines. This need has become greater with the increased use of shrinkproofed materials. An AATCC Accelerotor abrasion tester with some modifications has been found to give reproducible shrinking of wool materials in times of the order of several minutes. It is not claimed that the idea is original, as this machine was used by Pardo [2] in work connected with resin impregnation of fabrics. However, this investigation is primarily concerned with the tester's relationship to domestic washers.

Experimental

Instrument

Preliminary investigations showed that while the Accelerotor, as supplied, gave promise as a shrinkage tester, it suffered from two disadvantages: (i) the sample under test tended to be caught either around the blade of the propeller or between it and a ferrule covering the drive shaft, and (ii) at the relatively low speed found necessary for this work the motor had not sufficient power to maintain constant speed under the fluctuating load.

A modified rotor was made, basically similar to the S-shaped propeller supplied, but in which the blades were curved away from the direction of rotation. The separate ferrule was replaced by a conical hub formed integrally with the blades (Figure 1). Not only did this modification largely eliminate capture of the sample by the rotor, it allowed the maximum speed to be increased from 1000 to 1500 r.p.m., and considerably reduced speed fluctuations. It was thus possible to continue the work using the original motor.

Samples

Cloth samples were cut to 100 mm. squares with their sides at an angle of 45° to the warp and weft directions. Excessive fraying was prevented by sewing a wide zig-zag stitch about 7 mm. from the edge, and four small single stitches with their ends tied served as measuring marks.

To ensure that only felting shrinkage was measured, samples were relaxed for five min. in soap solution having an initial temperature of 60° C., followed by gentle rinsing in softened water. In order that they should lie flat but unstrained during measurement they were held down by a piece of Perspex slotted in the form of a cross to expose the marking stitches. After relaxation all fabrics were kept wet, and all measurements were made with the sample under water. Some of these procedures were based on work by Carter and Grieve [1] on felting in the Wash Wheel.

Method

No exhaustive investigation was made of optimum conditions of operation, but good results were ob-

[1] American Association of Textile Chemists & Colorists. Manufactured by Atlas Electric Devices Co., Chicago, U.S.A.

tained using those set out below:

Machine:	Accelerotor fitted with ribbed rubber liner and modified rotor.
Soap solution:	0.05% sodium oleate +0.3% sodium metasilicate in deionized water.
Solution volume:	400 ml.
Speed:	1,500 r.p.m.
Time of test:	5 min.
Temperature:	Ambient.

The several departures made from these conditions were found to decrease felting efficiency. At higher speeds, centrifugal force caused the soap solution and sample to be thrown to the periphery of the drum. Samples much exceeding 100 × 100 mm. in size tended to jam in the drum, causing large fluctuations in speed. The use of smaller volumes of soap solution also reduced felting action. In this case the suds were observed to be "stiffer" and the increased cushioning effect of such suds is considered to be the cause of the reduction. This effect was also described by Carter and Grieve [1].

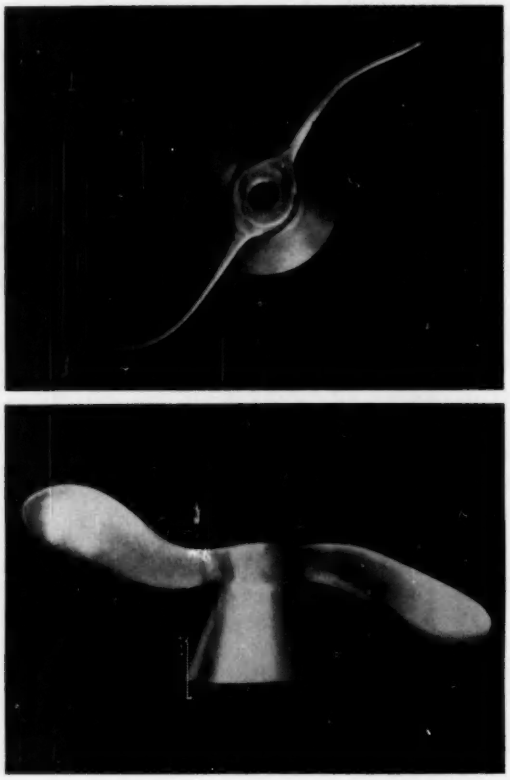


Fig. 1. Two views of the modified rotor.

A number of fabrics, both worsted and woolen, were felted in the modified Accelerotor and in three basically different types of domestic washing machine: (1) rotating drum (Bendix, Model LA.1.); (2) agitator (Simpson, Model AD4.); and (3) impeller (Hoover, Model 3174). The characteristics of the fabrics used are set out in Table I. Six pieces of each fabric were used in each test. In the case of the washing machines, all samples were washed together, small pieces of cotton cloth being added to make up the recommended medium load.

It must be emphasized that these machines are used here as test devices and not according to the manufacturers' recommendations. To eliminate the effects of any action other than washing, i.e., rinsing and spin drying, automatic machines were adapted for continuous washing. Washes were carried out at room temperature because of the difficulty of maintaining elevated temperatures constant over long periods. Sufficient commercial soap powder was used to form a moderate amount of suds. The actual amount of powder was different for each machine.

Results and Discussion

The following washing times were necessary to achieve shrinkages of the same order of magnitude as those reached after five min. in the Accelerotor:

Rotating drum machine:	7 hr.
Agitator machine:	4 hr.
Impeller machine:	2 hr.

Results of this survey are presented in Table II, all shrinkages being expressed as percent reduction in area. For greater clarity the samples have been arranged in order of increasing Accelerotor shrinkage values.

Despite some scatter in results it can be seen from Table II that there is appreciable correspondence in shrinkage values given by the Accelerotor with those of each of the washing machines, and the correlation diagrams in Figure 2 indicate the degree of this correspondence. Correlation coefficients for the data were also calculated and are presented in Table III. Tests of significance showed that in the case of the worsted fabrics the correlations were significant at the 5% probability level. For the

TABLE I. Characteristics of Cloths Used in Shrinkage Survey

Sample	Cloth type	Cloth weight, oz./lin.yd.	Ends/in.	Picks/in.	Yarn count
1	Worsted 2 × 2 twill	13	64	64	2/36
2	Worsted 2 × 2 twill	13½	68	68	2/36 warp 1/18 weft
3	Worsted 3 × 2 venetian	17½	100	60	2/36
4	Worsted soltine	13	38	54	2/36*
5	Worsted 2 × 2 hopsac	17½	65	61	2/36
6	Worsted 2 × 2 twill	11	53	56	2/36 warp 1/18 weft
7	Worsted 2 × 2 gaberdine	14	88	57	2/40
8	Worsted 2 × 2 twill	13	64	62	2/36
9	Woolen fancy weave based on hopsac	11½	28	24	1/12
10	Woolen plain weave	8	38	30	1/30
11	Woolen hopsac	10½	28	26	1/28
12	Woolen plain weave	12½	44	41	1/28
13	Woolen plain weave	8	26	24	1/12

* Every alternate end 2/36 doubled.

woolen materials the correlation was not as definite, significances being in the region of the 10% level, but this is probably due to the smaller number of fabrics used in the test.

The regression lines in Figure 2 are not intended to represent quantitative relationships between the Accelerotor and the washing machines concerned; a much more detailed survey would be needed before such relationships could be used with any degree of precision. A broader survey may also show that the correlation is not linear, as shown here, but curvilinear and embracing both worsted and woolen values. However, it is indicated that this type of machine and procedure could become a suitable standard test for felting shrinkage in wool fabrics.

The time dependence of shrinkage in the Accelerotor was measured on a worsted sample (No. 3) and a woolen sample (No. 10). The results are plotted in Figure 3, each point being the mean of four determinations. The fact that the values closely follow a smooth curve is an indication of a satisfactory shrinkage–time relationship.

In a practical tester based on the Accelerotor, several further modifications appear to be desirable.

TABLE II. Area Shrinkages of 13 Fabrics Felted in the Accelerotor and in 3 Domestic Washing Machines *

	Accelerotor		Rotating drum (7 hr.)		Agitator (4 hr.)		Impeller (2 hr.)	
Sample	Shrinkage, %	Std. Error	Shrinkage, %	Std. Error	Shrinkage, %	Std. Error	Shrinkage, %	Std. Error
6	11.3	1.0	2.7	0.2	2.2	0.1	2.6 [5]	0.4
8	14.2	0.4	8.6	0.3	3.9 [5]	0.2	7.1 [5]	0.2
7	17.6	0.4	8.3	0.4	3.7	0.5	8.1 [5]	0.3
5	20.6	0.3	8.8	0.4	5.9	0.6	11.5	0.3
3	20.8	0.3	11.2	0.2	7.1	0.2	12.4	0.3
1	23.6	0.2	13.0	0.4	8.3	0.2	12.6	0.6
4	24.6	0.3	11.9	0.9	7.4	0.3	13.3	0.7
2	25.0	0.2	14.4	0.5	7.7 [4]	0.4	12.8 [3]	0.2
12	33.1	0.4	22.4	0.4	17.8	0.3	25.0	0.5
13	43.7	0.7	41.8	0.7	33.0	1.0	36.1	1.1
10	45.7 [4]	0.3	43.0	0.6	29.8	0.6	34.5	0.9
9	49.8	0.5	48.9	0.7	39.0 [5]	0.7	45.9	0.5
11	51.5	0.5	50.1	0.5	39.8	0.7	45.1	1.2

* Values are mean shrinkages of 6 test pieces except where indicated in brackets.

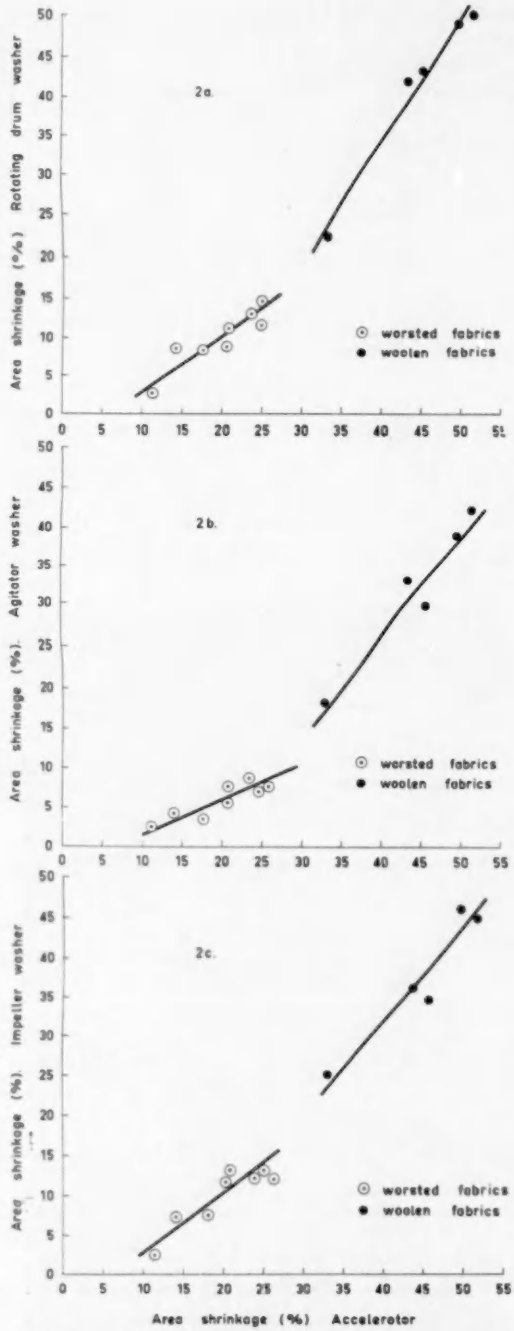


Fig. 2. Shrinkage correlation diagrams: (a) Accelerotor vs. rotating drum washer; (b) Accelerotor vs. agitator washer; and (c) Accelerotor vs. impeller washer.

TABLE III. Correlation Coefficients Calculated from the Data Given in Table II.

Correlation	Correlation coefficient: Worsted, 8 fabrics	Correlation coefficient: Woolen, 5 fabrics
Accelerotor—rotating drum	+0.806	+0.827
Accelerotor—agitator	+0.831	+0.785
Accelerotor—impeller	+0.876	+0.787

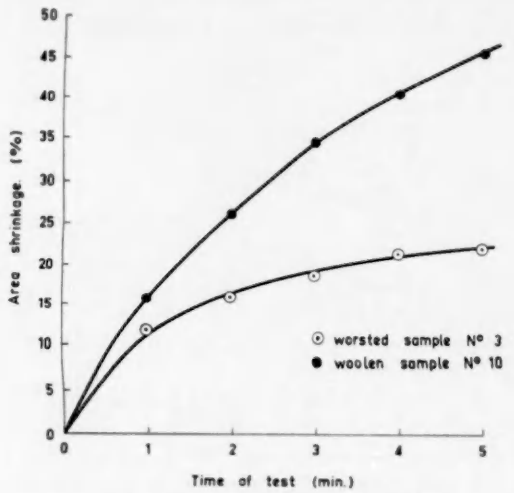


Fig. 3. Time dependence of shrinkage in the modified Accelerotor.

There is no apparent necessity for variation in rotor speed, so that the variable-speed motor and tachometer could well be replaced by a motor of higher power, which, in order to speed up test schedules, should be capable of driving a suitable number of drums simultaneously. Another desirable feature would be the incorporation of an accurate timing device to stop the motor after the desired test time had elapsed.

The work described in this paper has been devoted to normal fabrics. Investigations into the usefulness of the modified Accelerotor in the field of shrinkproofed materials are at present in progress.

Literature Cited

1. Carter, E. G. H. and Grieve, W. S. M., *Wool Industries Research Association Special Publication* No. 6 (1954).
2. Pardo, C. E., *J. Textile Inst.* **51**, T1462 (1960).

Manuscript received April 17, 1961.

Letters to the Editor

A Preliminary Study of a Technique for Measuring Flexural Vibrations in Fabrics[1, 2]

Department of Textile Industries
Manchester College of Science and Technology
University of Manchester
Manchester 1, England

To the Editor
Textile Research Journal

Dear Sir:

As a further development of work on the physical properties of fabrics, an investigation of dynamic properties was suggested. While there are various possible modes of vibration of a fabric specimen, the simplest to study experimentally and theoretically is the bending vibration. There are few, if any, references to the study of fabric vibrations in the literature, although there is an extensive record of work on fiber vibrations, which has been reviewed by Meredith [4, 5]. There are many experimental and theoretical discussions of mechanical vibrations in general [1, 6, 8].

The present note describes the results of a preliminary study of a technique for measuring flexural vibrations in fabrics which has given some useful results and pointers to future work.

Theory

The general formula for flexural vibrations [1] may be written

$$\nu = \frac{1}{2\pi} 3.52 \left(\frac{EI}{\mu l^4}\right)^{\frac{1}{2}} \qquad (1)$$

where ν = resonant frequency for fundamental vibration, cycles/sec.
E = modulus, dyne/cm.^{2}
I = moment of inertia of cross section, cm.^{2}
μ = mass per unit length of specimen, g./cm.
l = length of specimen, cm.

For vibrations, other than the fundamental, different numerical constants are applicable. Also, if there is strong damping a correction should be applied [5].

The relevant parameters for applying this formula to fabrics are given by Peirce [7]. Considering unit width of fabric, we have

$G = EI/g$ = flexural rigidity, g.-wt.-cm.

$w = \mu$ = mass per unit area, g./cm.^{2}

Substituting, this gives

$$\nu = \frac{1}{2\pi} 3.52 \left(\frac{Gg}{wl^4}\right)^{\frac{1}{2}}$$

$$= 17.55 \frac{(G/w)^{\frac{1}{2}}}{l^2} \qquad (2)$$

Experimentally this resonant frequency may be found by observing the maximum amplitude of forced vibrations imposed over a range of frequencies. At zero frequency there is a static deflection, which in a simple system increases to a maximum at the resonant frequency and then decreases steadily to zero.

The damping of the vibrations is given by

$$\text{loss factor} = \tan \delta = \Delta\nu/\nu \qquad (3)$$

where $\Delta\nu$ = bandwidth, for amplitude = maximum/$\sqrt{2}$.

The above analysis assumes that the vibration is controlled only by the forces involved in flexing the fabric. In reality, there will also be gravitational forces acting on the mass of the fabric. It can be shown that the relative effects of these two types of controlling forces are given approximately

[1] This work was carried out during a stay of three months at the Swedish Institute for Textile Research (TEFO) and, despite the preliminary nature of the investigation, it was felt useful to put the experience on record for the benefit of others, since there is no immediate prospect of it being continued by the authors or by others at TEFO.

[2] Editor's note: Although this contribution exceeds our usual requirements regarding the length of a Letter to the Editor, it is published in this manner because of the preliminary character of the investigation being discussed.

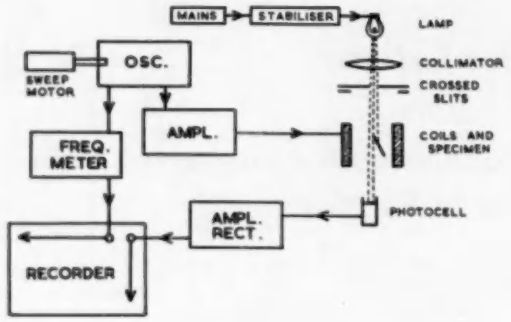


Fig. 1

by the ratio

$$\frac{\text{potential energy due to mass of fabric}}{\text{energy stored in bending}} = \frac{wl^3}{3G} \quad (4)$$

For the effect of the mass of fabric to be negligible it is necessary that $(wl^3/3G) \ll 1$. Similarly if an added mass m g./cm. is placed at the base of the fabric specimen, it can be shown that it will have a negligible effect provided $m \ll (3G/2l^2)$.

Numerical values based on Equations 1 and 4 show that it is necessary to use fairly short specimens (of the order of 1 cm. in length) in order to keep the effect of the fabric mass negligible, but they should not be too short or the resonant frequencies will be inconveniently high. In addition, if the length becomes so short that only a few cross threads are included in the specimen, then the characteristic fabric behavior will be lost.

Experimental Details

The experimental method was due to Dr. B. Drake [2]. Samples are excited by the force acting on a small piece of iron fixed to the base of the specimen when it is placed in an alternating electromagnetic field. Figure 1 is a block diagram of the electrical circuits used. The coils of an electromagnet are supplied with current from an oscillator through an amplifier. The frequency of the oscillator is swept over the desired range by means of the change of capacity in a variable condenser rotated by a motor. The frequency is measured by a frequency meter which operates the x-direction of an xy-recorder. Calibration frequencies can be fixed by marking the trace, when appropriate Lissajous' figures are observed on an oscilloscope connected to the oscillator signal and to 50 cycles/sec.

The specimen partially obscures a rectangular beam of parallel light which is falling on a photocell. When the specimen is vibrating, the photocell will generate an alternating signal, which after amplification and rectification is fed to the y-direction of the recorder. A curve of amplitude against frequency is consequently plotted.

The equipment operates over four frequency ranges, with maxima of approximately 5, 20, 80, and 200 cycles/sec. Each range includes zero frequency on the chart, but cannot be used to plot results below about 10% of the maximum frequency of the range.

The fabric specimens were usually cut 1 cm. wide and 5 cm. long, and 1 cm. of fine iron wire (of mass 0.0055 g./cm.) was stuck across one end of the piece of fabric.[3] The specimen was then mounted in a brass clamp having one face lined with rubber, so that the desired length of fabric projected from the clamp.

The plane of the fabric was placed at a slight angle to the beam of light, so that in the rest position half of the beam was blocked by half of the fabric. Displacement of the fabric by bending causes the amount of light transmitted to increase or decrease.

The light beam comes from a lamp with stabilized voltage supply, is made parallel by a lens, and is then restricted by crossed slits to a rectangular beam of dimension 0.2 cm. × 0.4 cm.

The fabrics were taken from the TEFO collection, and are listed in Table I, together with values of parameters reported for static tests by Lindberg et al. [3], who also give other details of the fabrics.

The humidity and temperature of the room were not controlled (although this would be necessary in a full investigation of bending vibrations), but measurements of these quantities were made at intervals.

Typical Results: Sources of Error

The curves obtained were often distorted and differed from ideal resonance curves. The reasons for the distortions are as follows.

1. The current supplied to the coils of the electromagnet varied to some extent as the frequency changed, thus altering the driving force.

[3] This would have a 1% effect with 1.0 cm. specimens when $G = 0.4$, and a 10% effect when $G = 0.04$.

TABLE I. Fabrics Tested and Summary of Results

Fabric No.	Type	Static test results [1, 3]					Dynamic test results							
										Bending		Torsion		
		G, g.-wt.-cm.	W, g./cm²., $\times 10^{-4}$	G/w	γ, deg.	γw $\times 10^{-4}$	RH, %	Temp., °C	l, cm.	ν, c/s	δ	ν, c/s	δ	G/w calc'd.
1227	Cotton	0.039	129	3.0	7.4	955	68	22	1.0	42	0.15	86	0.25	5.7
1200	Cotton	0.081	151	5.3	2.7	408	57	20	1.0	77	0.21	185	—	19
1228	Cotton	0.17	160	10.7	0.18	29	62	22	1.0	67	0.13	178	—	14
1189	Cotton	0.33	217	15.2	2.4	521	72	21	1.0	46	0.15	167	—	6.9
1245	Cotton	0.16	97	16.5	0.98	95	61	21	1.0	26	—	97	0.23	2.2
1238	Cotton	1.8	403	44.7	0.11	44	57	19	2.0	67	0.16	—	—	234
1242	Cotton	1.2	248	48.4	0.18	45	58	21	2.0	42	0.19	—	—	92
1206	Wool	0.024	203	1.18	16	3248	73	22	1.0	34	0.19	106	—	3.8
1207	Wool	0.021	127	1.65	27	3429	60	19	1.0	27	0.19	69	0.23	2.4
1208	Wool	0.049	206	2.4	18	3708	50	20	1.0	43	0.14	100	0.23	6.0
1201	Rayon staple	0.067	177	3.8	4.0	708	61	22	1.0	33	0.14	76	0.16	3.5
1205	Rayon staple	0.24	250	9.6	9.7	2425	63	22	1.0	36	0.12	75	0.18	4.2
1248	Rayon staple	0.17	79	21.5	36.0	2844	60	20	1.0	34	0.12	92	0.25	3.8
1224	Acet. fil.	0.18	97	18.6	5.2	504	62	22	1.0	44	0.12	116	0.11	6.3
1225	Perlon fil.	0.12	138	8.7	3.3	455	71	20	1.0	—	—	150	0.17	—
1221	Nylon fil.	0.011	48	2.3	20	960	58	20	1.0	19	0.22	72	—	1.2
1220	Nylon fil.	0.075	149	5.0	8.8	1311	57	20	1.0	37	0.16	118	0.33	4.5
1223	Orlon fil.	0.009	84	1.07	4.6	386	70	21	1.0	48	0.17	112	0.17	7.5
1222	Silk	0.006	31	1.94	49	1519	51	22	1.0	14	0.15	51	0.10	0.6
1251	Saran	1.7	378	45.0	0.49	185	50	20	2.0	85?	—	—	—	
1254	R/C/N (nonwoven)	1.6	85	188	0.19	16	65	22	2.0	45	0.14	—	—	105
1215	W/RF	0.31	236	13.1	22	5192	61	20	1.0	55?	—	115	0.31	
1239	C/L	—	341	—	3.1	1057	61	20	1.5	45	0.17	65	0.21	33
1213	S/W	0.085	125	6.8	9.3	1162	57	20	1.0	28	0.16	81	0.30	2.5

2. Torsional vibrations were present as well as bending vibrations. The resonant frequencies for torsion were higher than for bending, but sometimes the lower parts of the torsion peak overlapped parts of the bending peak. It was found impossible to eliminate the tendency to excite torsional oscillations, which were commonly of larger amplitude than the bending vibrations.

3. Harmonics were present in the current fed to the coils of the electromagnet due to appreciable departures from a pure sine-wave form, so that the torsional or bending vibrations could be excited at lower apparent driving frequencies when a harmonic of the appropriate frequency was present. This gives rise to additional smaller peaks, which are superimposed on the main curve.

These effects may cause errors in the calculations of the resonant frequency and damping by shifting the position and magnitude of the maximum and by altering the bandwidth at the maximum/$\sqrt{2}$ level. They may also make it difficult to determine the true base line, which lies above the electrical zero, because of the occurrence of stray signals. In order to find the true base line, it is necessary for the vibration to fall to negligible amplitude above the resonant frequency (since below the resonant frequency, the static deflection determines the position), and this does not always occur. Some of these effects are illustrated diagrammatically in Figure 2, and typical curves are shown in Figures 3 and 4.

With some specimens, a markedly asymmetrical trace was obtained, usually in torsional vibrations of the type shown in Figure 5. When observed visually, the vibration showed a sudden cut-off when the frequency reached a critical value. The unstable behavior is typical of nonlinear deforma-

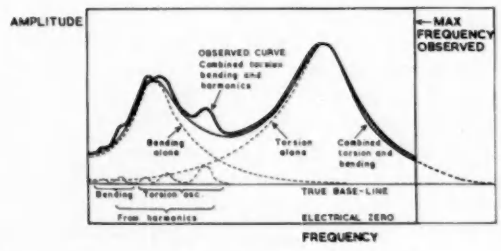


Fig. 2

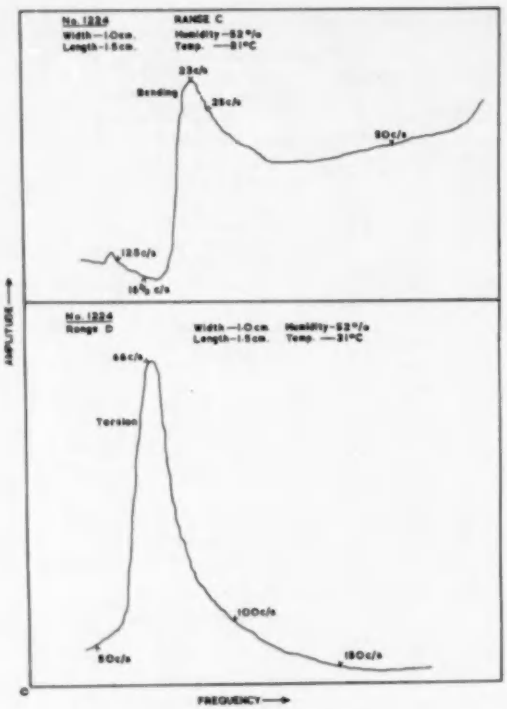


Fig. 3

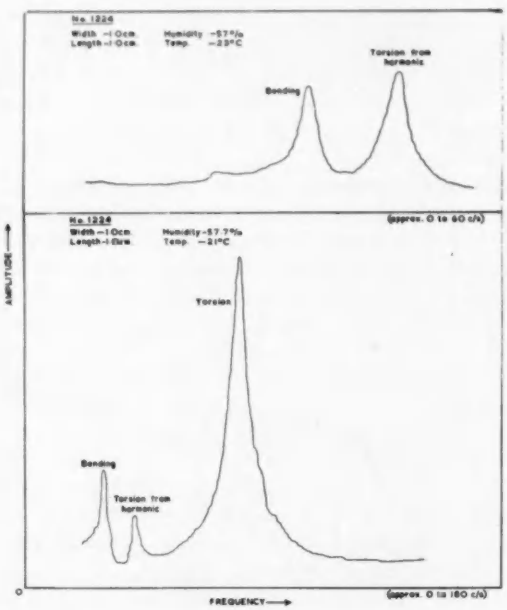


Fig. 4

tion, and the curves are similar to theoretical curves shown by van Santen [8]. The form of curve differs according to whether the frequency is rising or falling during the test.

Because the experimental curves are distorted for these various reasons, estimates of resonant frequency and damping must be subject to error. In calculating the latter parameter it has been necessary to make rough personal judgments of the position of the true base line and of the true form of the undistorted curve. Where the peak is very asymmetrical, the steeper side has been regarded as giving the best indication of damping: a typical example is shown in Figure 6.

Effect of Specimen Length and Other Factors

Three specimens (1224, 1205, and 1208) were tested over a range of lengths, and a typical graph of resonant frequency against $1/l^2$ is shown in Figure 7. According to Equation 2, the points for bending vibrations should fall on a straight line through the origin with a slope of $17.55\ (G/w)^{\frac{1}{2}}$. In fact, the points lie on curves.

It was thought that the deviation from linearity might be due to an end effect. If the actual length involved in the vibration was equal to the measured length, l, plus an end correction, ϵ, we should have

$$\nu = 17.55\ \frac{(G/w)^{\frac{1}{2}}}{(l+\epsilon)^2} \tag{5}$$

Rearrangement of this expression gives

$$\frac{1}{\nu^{\frac{1}{2}}} = \frac{l+\epsilon}{(17.55)^{\frac{1}{2}}(G/w)^{\frac{1}{2}}} \tag{6}$$

When $1/\nu^{\frac{1}{2}}$ is plotted against l, as in Figure 8, the points do fall on straight lines, provided the lengths

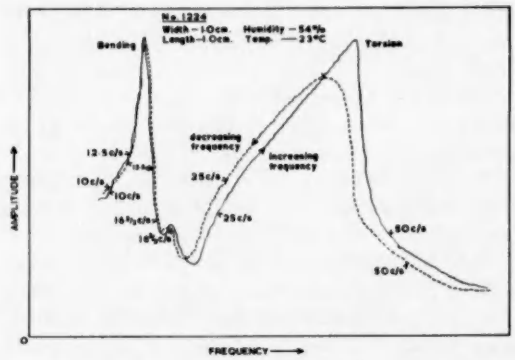


Fig. 5

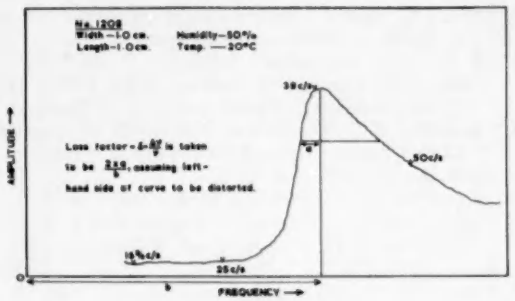


Fig. 6

of specimens are not too long. Values of the slope, G/w, and the end correction are given in Table II. For lengths greater than 1.5 cm. in Specimen 1205 and 1208, the experimental points deviate from the straight line.

A few tests were made with specimens only 0.5 cm. wide, but there was no appreciable difference from results with specimens 1.0 cm. wide.

Some tests were also made with shorter pieces of iron wire on the specimen, but again no appreciable difference was found.

Comparison of Fabrics

Values of resonant frequencies and loss factors are given in Table I for the range of fabrics tested, together with calculated values of G/w for the dynamic tests.

There is little correlation between the static and dynamic values of G/w. One possible cause of the differences in static and dynamic behavior may be associated with the time required for the fibers and yarns to slide over one another.

Values of the loss factor in the bending vibrations range from 0.11 to 0.22, but no particular trends are obvious within the limited range of fabrics tested, though some significant correlations might be discerned by those more familiar with other differences among these fabrics.

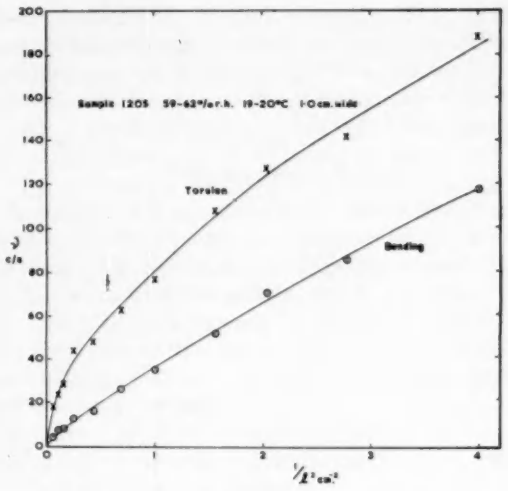


Fig. 7

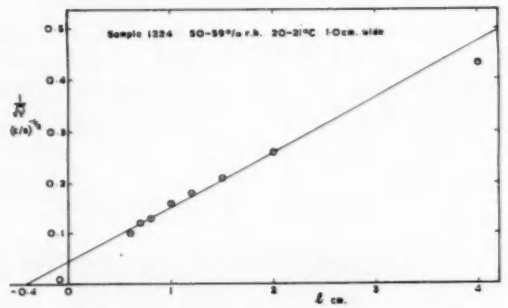


Fig. 8

TABLE II

Fabric No.	Width, cm.	Slope of $1/\nu^2$ against l	G/w calc'd	G/w static test	End correction, cm.
1224	1.0	0.112	20.6	18.6	0.4
1224	0.5	0.112	20.6	18.6	0.2
1205	1.0	0.146	4.1	9.6	0.15
1208	1.0	0.142	8.0	2.4	0.1

Conclusion

This preliminary study of the technique has shown that the flexural behavior of fabrics can be studied dynamically and would form a useful part of a wider study of fabric properties. The difference between values of flexural rigidity in static and dynamic tests merits further investigation. The amount of damping should also be of interest and should be compared with damping in the fibers themselves. Shear vibrations would also be of interest, although they will be more difficult to produce experimentally. The torsional vibrations, which are very easily excited, would also be of interest if their theory can be developed.

For further experiments, some refinements of technique would be desirable. The avoidance of harmonics in the oscillation cycle is important. If possible the torsional vibrations should be elimi-

nated. This might be done by driving one end of the sample from a mechanical vibrator, leaving the other end free. The influences of air damping should be checked, either experimentally or theoretically.

Acknowledgments

The work was carried out during the three months tenure at the Swedish Institute for Textile Research (TEFO) of an O.E.E.C. Senior Visiting Fellowship (J.W.S.H.) and a travelling scholarship (D.J.T.). Our thanks are due to Professor N. Gralén, Lic. B. Olofsson, Lic. B. Behre, and others at TEFO for suggesting the problem and for their advice and help. The experimental equipment was made available by the Swedish Institute for Food Conservation Research (SIK), and we are very grateful to the Director for giving us permission to work at SIK, and to Dr. B. Drake and Mr. K. Remi for a great deal of practical assistance and advice.

Literature Cited

1. Den Hartog, J. P., "Mechanical Vibrations," New York, McGraw-Hill, 1956.
2. Drake, B., Swedish Institute for Food Conservation Research, personal communication.
3. Lindberg, J., Bernskiold, A., Behre, B., and Dahlberg, B., *Offenligt Meddelande, TEFO*, No. 18. To be submitted to TEXTILE RESEARCH JOURNAL.
4. Meredith, R., "Mechanical Properties of Textile Fibres," Amsterdam, North-Holland Publishing Company, 1956, pp. 123 ff.
5. Meredith, R., in: "Physical Methods of Investigating Textiles," Meredith, R. and Hearle, J. W. S., ed., New York, Textile Book Publishers, 1959, pp. 237 ff.
6. Morse, P. M., "Vibration and Sound," 2nd ed., New York, McGraw-Hill, 1948.
7. Peirce, F. T., *J. Textile Inst.* **21**, T377 (1930).
8. Santer, G. W. van, "Introduction to a Study of Mechanical Vibrations," Eindhoven, Philips' Technical Library, 1953.

J. W. S. HEARLE,
Department of Textile Industries,
Manchester College of Science and Technology,
University of Manchester,
England

and

D. J. TURNER,
Department of Textile Technology,
Royal College of Science and Technology,
Glasgow, Scotland

Observations on the State of Supercontracted Wool

C.S.I.R.O. Wool Research Laboratories
Division of Textile Physics
Ryde, Sydney, Australia
June 23, 1961

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

One would expect supercontracted and therefore disorganized wool fibers to show a greater length swelling due to water uptake than normal fibers. A normal Corriedale wool fiber swells longitudinally by approximately 1.2% [2] over the range of moisture content from dryness to saturation. The corresponding diametral swelling is approximately 16% [6].

In an attempt to determine whether supercontracted wool approaches isotropy we have examined the swelling properties of fibers which had, after contraction in 8 *M* LiBr solution and washing in water, reached a length less than their natural length. Normal, reduced, and reduced and methylated Corriedale wools were used.

A number of wool samples were reduced, each to a different extent, in thioglycollic acid at pH 5 and 37° C. Subsamples were taken, and the remainder of each sample treated with methyl iodide solution at pH 7.5 and 37° C. for 18 hr. Cystine contents were determined for methylated samples only. Supercontraction was produced using 8 *M* LiBr solution at a number of different temperatures, but none exceeding 100° C. As demonstrated by Griffith and Alexander [1] the degree of contraction which remains in normal fibers, after similar treatment and washing in water, can be changed by interrupting the contraction at suitable times. We have found that this is true for reduced fibers, and by these means fiber snippets were prepared which showed a range of contractions.

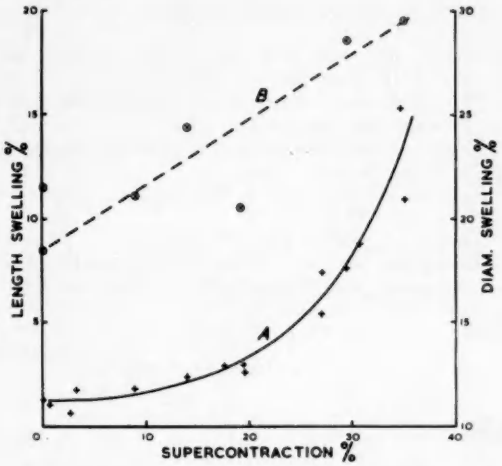


Fig. 1. Curve A: length swelling (ordinates at left) of variously treated Corriedale wool fibers (due to a moisture content change from dryness to saturation) plotted against percentage supercontraction after washing. Curve B: diametral swelling values (ordinates at right) for some of the samples which yielded the data of Curve A.

Lengths and diameters of the snippets were measured in the water-saturated state and in the dry state. The results are shown in Figure 1 where in curve A longitudinal swelling is plotted against degree of contraction after washing. Each point on the graphs represents a mean value from 6–8 snippets. All points are fairly closely distributed about a smooth curve despite great differences in snippet preparation. The major differences were (a) disulfide losses ranged from 0 to 72%; (b) room temperature, 35° C., 50° C., and 100° C. were used for supercontraction; (c) snippets were taken from normal, reduced, and reduced and methylated fibers. This is in accord with the idea that if damage is chiefly a disorganization of the keratin, the state of the fiber will depend on the degree of contraction and not on how it was produced.

It will be seen that longitudinal swelling increases slowly at first and starts to increase rapidly when the degree of supercontraction, after washing, is 20–25%. The swelling rises to a value of approximately 15% at maximum contraction. This is close to the value of diametral swelling for untreated wool.

However, curve B of Figure 1 indicates that the corresponding diametral swelling also increases and reaches a value of about 30%. Because there was no control over rotation of the snippets the possible error in these values is much larger than in the case of length swelling. The values are again the means of 6–8 measurements.

It appears that swelling is not isotropic in fully contracted wool fibers.

Further evidence on the same point came from X-ray diffraction studies of supercontracted wool. Samples containing 50–100 aligned fibers of normal (Sample 0), reduced (Sample 11a) and reduced and methylated (Sample 11b) wools were treated in 8 *M* LiBr solutions at 100° C. Sample 11b, on analysis, showed a disulfide loss of 70%. Before treatment in the LiBr solution all samples gave similar high-angle X-ray diffraction photographs, the only visible difference being that the 5.1 Å arc from 11a and 11b was slightly more diffuse than from the normal wool. While the samples were in 8 *M* LiBr solution no discrete X-ray reflections could be seen [4].

In each case full contraction (~35%) was achieved in the LiBr solution. While still in this solution Sample 11a lengthened [3] until it approached the natural length. Samples 0 and 11b did not increase their length. All samples were washed in water and steeped in a large volume of water for 16 hr. They were then brought to room conditions, and X-ray diffraction photographs were obtained.

All samples showed a distinct, oriented 5.1 Å re-

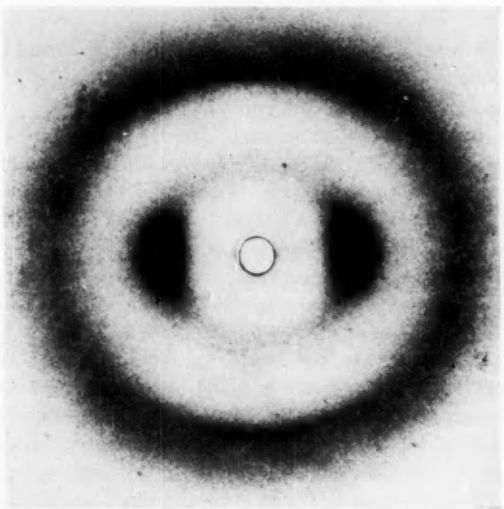


Fig. 2. An example of the high-angle X-ray diffraction pattern of wool which has been treated in LiBr solution at 100° C., washed, and brought to room conditions. This sample was reduced and methylated prior to treatment in LiBr solution; disulfide loss was 70%.

flection, and an arced 9.8 Å reflection (see Figure 2). However, the 5.1 Å reflection could not be seen when the samples, during X-ray, were kept wet with liquid water wicking into them.

It is concluded that organized structures are present in supercontracted and washed wools at room conditions of temperature and humidity. The phenomenon is probably similar to that reported by Sikorski [5] who found that the α-pattern could be obtained from denatured keratin by the action of various reagents. In our case the conditions yielding α-recovery are milder.

We thank Dr. S. J. Leach for the cystine analyses.

Literature Cited

1. Griffith, June and Alexander, A. E., TEXTILE RESEARCH JOURNAL **27**, 755 (1957).
2. Haly, A. R. and Feughelman, M., TEXTILE RESEARCH JOURNAL **31**, 135 (1961)
3. Haly, A. R. and Feughelman, M., TEXTILE RESEARCH JOURNAL **30**, 365 (1960).
4. Haly, A. R. and Snaith, J. W., *Biochem. et Biophys. Acta* **44**, 180 (1960).
5. Sikorski, J., *Nature* **170**, 275 (1952).
6. Wool Industries Research Association, Leeds, "Wool Research," Vol. 2, 13 (1955).

A. R. HALY
J. W. SNAITH

Graft Polymers of Cotton Cellulose and Acrylonitrile Initiated by Radiation

Southern Regional Research Laboratory [1]
1100 Robert E. Lee Boulevard
New Orleans 19, Louisiana
July 7, 1961

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

It has been previously reported that interaction of polyacrylonitrile with cotton cellulose can be induced by high-energy gamma radiation [1–3, 8]. Although the products contained large amounts of polyacrylonitrile which were not extracted by N,N-dimethyl formamide, the nature of the interaction was not definitely established, that is, whether homopolymerization and/or graft polymerization had occurred. Purified and cyanoethylated Deltapine cotton yarns were interacted with acrylonitrile monomer by application of the monomer to the cotton and by polymerization of the monomer initiated either by ceric ion redox systems [4–6] or by high-energy gamma radiation from cobalt-60. In typical experiments using the ceric ion redox system, one part of cotton cellulose was immersed in 30 parts of an aqueous solution, 0.005 *M* in ceric ammonium nitrate and 0.05 *M* in HNO_3, at 25° C.; then 1.2 parts of acrylonitrile monomer was added; after 60 min. the cellulose was removed from the solution and rinsed with water. In typical experiments using high-energy radiation, the cotton yarns were immersed in a solution containing 32 parts of acrylonitrile monomer in 68 parts of aqueous 80% $ZnCl_2$, padded to give about a two- to fourfold increase in weight of the original yarn, and then irradiated. The resulting products were extracted with N,N-dimethyl formamide at 25° C. to remove the weakly interacted monomer and polymer from the yarns. The polymer content was calculated from the unextractable nitrogen content as previously described [1, 3].

The solubility of the cellulose of the products in 0.5 *M* cupriethylene diamine at 25° C. and infrared spectral data [7] for the products are given in Tables I and II. There was a large decrease in the solubility of cellulose of purified cotton containing polymer, where polymerization had been initiated by radiation. The solubility of cellulose of purified cotton containing polymer, where polymerization had been initiated by ceric ion, was approximately zero. The solubility of cellulose of cyanoethylated cotton containing polymer, where polymerization had been initiated by radiation was also approximately zero.

The optical density at the principal absorption bands of the infrared spectrum of unmodified cotton [7] is shown for purified and cyanoethylated cottons in Table I. The OH band intensities of these prod-

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

TABLE I. Infrared Spectral Data of Graft Polymers of Cotton and Acrylonitrile

Cotton product*	Solubility of cellulose,† %	Optical density/mg. product: 2.8–3.4 μ O—H stretching	3.4 μ C—H stretching	4.45 μ C≡N stretching	7.25 μ C—H deformation	8.6 μ C—OH deformation
A	99	0.534	0.213	0.000	0.281	0.457
B	30	0.254	0.118	0.064	0.170	0.250
C	0	0.280	0.166	0.046	0.168	0.248
D	97	0.304	0.150	0.052	0.202	0.315
E	0	0.209	0.103	0.069	0.143	0.209

* A: purified cotton. B: purified cotton, irradiated 1.0 megaroentgen, containing 30% polymer. C: purified cotton, ceric ion initiated, containing 25% polymer. D: cyanoethylated cotton, DS 0.67. E: cyanoethylated cotton (0.69 DS), irradiated 0.8 megaroentgen, containing 38% polymer. (Note: Solubilities of irradiated purified and cyanoethylated cottons were the same as A and B.)

† Solvent: 0.5 *M* cupriethylene diamine.

TABLE II. OH Band Intensities of Graft Polymers of Cotton and Acrylonitrile

Cotton product*	2.8–3.4 μ O—H stretching	8.6 μ C—OH deformation
	optical density/mg. cellulose	
A	0.534	0.457
B	0.363	0.357
C	0.373	0.331
D	0.371	0.384
	optical density/mg. cyanoethylated cellulose	
D	0.304	0.315
E	0.337	0.337

* See * in Table I.

ucts are compared in Table II on the bases of their contents of cellulose and cyanoethylated cellulose. There were decreases in the OH band intensities of purified cotton cellulose (A) on interaction with polyacrylonitrile initiated by ceric ion (C) or by radiation (B) and on cyanoethylation of the cellulose (D). There was not a significant change in the OH band intensities of cyanoethylated cotton (D) on interaction with polyacrylonitrile initiated by radiation (E).

It was concluded that graft polymers of cotton cellulose and acrylonitrile have been made, as evidenced by (i) unextractable polymer add-on; (ii) decreased cellulose solubility; and (iii) decreased OH band intensities for cotton, indicating grafting induced at the OH group on the cellulose molecule. In the case of cyanoethylated cotton, the relative constancy of the OH band intensities probably indicated grafting at the cyanoethyl group.

Literature Cited

1. Arthur, J. C., Jr. and Demint, R. J., TEXTILE RESEARCH JOURNAL **30**, 505–509 (1960).
2. Arthur, J. C., Jr., Demint, R. J., McSherry, W. F., and Jurgens, J. F., TEXTILE RESEARCH JOURNAL **29**, 759 (1959).
3. Demint, R. J., Arthur, J. C., Jr., and McSherry, W. F., TEXTILE RESEARCH JOURNAL **31**, 821–824 (1961).
4. Mino, G. and Kaizerman, S., *J. Polymer Sci.* **31**, 242–243 (1958).
5. Mino, G. and Kaizerman, S., U. S. Patent 2,922,768 (January 26, 1960).
6. Mino, G., Kaizerman, S., and Rasmussen, E., *J. Polymer Sci.* **38**, 393–401 (1959).
7. O'Connor, R. T., DuPré, E. F., and McCall, E. R., *Anal. Chem.* **29**, 998–1005 (1957).
8. Rutherford, H. A., Armstrong, A. A., Jr., Kiser, L. H., and Kirby, R. D., TEXTILE RESEARCH JOURNAL **30**, 546 (1960).

JETT C. ARTHUR, JR.
ROBERT J. DEMINT

Some Aspects of the Reaction between Urea and Cellulose

Textile Application Laboratory
Rohm & Haas Co.
Philadelphia, Pa.
June 12, 1961

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

I should like to make two comments with respect to the recent paper by Segal and Eggerton [2]. First, they credit me with "private communications," which is quite understandable since we have corresponded at intervals since 1952 on various aspects of this subject. However, they have failed to acknowledge the contribution of D. D. Gagliardi, who carried out the original experiments with cupric chloride as catalyst for this reaction on both rayon and cotton [1]. Cupric chloride was the most effective catalyst of the many he tried.

Second, the authors' emphasis on the use of an *aqueous* solution of urea is misleading. It is true that water must be present in the padding solution, but this is primarily to permit penetration into the fibers. During the cure, the water evaporates and the reaction then occurs between the cellulose and the essentially anhydrous molten urea. In fact, presence of water during the cure inhibits the reaction. Ammonia, a byproduct of the reaction, also seems to lower the yield, as might be expected. These effects are illustrated in the following experiment, which was performed recently by E. O. J. Heiges of this laboratory.

Cotton (80 × 80 sheeting) was soaked for 10 min. in a 50% solution of urea containing 1.27% $CuCl_2 \cdot 2H_2O$, then squeezed to about 80% wet pickup. To ensure the presence of decreasing amounts of water during the reaction period, portions of the fabric were further handled, while still wet, as follows: (1) put into a Parr bomb half-filled with padding solution; (2) put into a bomb without additional solution; (3) air dried at room temperature, then put into a bomb; or (4) air dried at room temperature then further dried 5 min. at 240° F. before putting into a bomb.

The bombs were tightly sealed, then heated for 1 hr. at 300° F. For comparison, a portion of the same urea-treated fabric, dried as in (4) above, rather than being confined in a bomb, was heated 1 hr. at 300° F. in the circulating air of the large curing oven.

After heating, the fabrics were washed 1 hr. in running tap water, boiled 15 min. in de-ionized water, rinsed briefly, and dried. Subsequent nitrogen analyses gave the results shown in Table I.

Two effects are worth noting. First, as the amount of moisture was lowered, going from Case 1 to Case 4, the reaction yield increased. This is what we set out to determine. Although an aqueous padding solution was used, the water served no purpose other than to permit penetration of the urea into the cellulose.

Second, curing in the open air gave a much better yield than curing in a sealed container. Attempts to explain this are complicated by the fact that conditions in Case 4 were not completely anhydrous, as was shown by slight staining of the upper end of the fabric (that is, the end farthest from the hot base of the bomb). This is interesting, since the formation of cellulose carbamate does not involve the release of water. However, the amount of water did not seem great enough to account for the much lower yield in Case 4 as compared to Case 5. It is probable that ammonia, a byproduct of the reaction, must also be removed in order to obtain a good reaction yield.

In conclusion, the reaction between urea and cellulose appears to go best when there is nothing else present but the catalyst. Further, although no thor-

TABLE I. Effect of Reaction Conditions on Yield of Fixed Nitrogen

Conditions*	% N
1. Cured in Parr bomb in presence of excess padding solution	0.07
2. Freshly padded, no excess, cured in bomb	0.17
3. Air dried, then cured in bomb	0.35
4. Dried at 240° F., cured in bomb	0.44
5. Dried at 240° F., cured in large oven	1.60

* All cured 60 min. at 300° F.

ough study has been made, I believe that little reaction will take place below the melting point of the urea–catalyst mix. It is for these reasons that I hold to the view that the reaction involves molten urea—the urea being inside as well as outside the fibers.

Literature Cited

1. Gagliardi, D. D., unpublished data, Textile Applications Laboratory, Rohm & Haas Co. (1951).
2. Segal, L. and Eggerton, F. V., Textile Research Journal **31**, 460 (1961).

A. C. Nuessle

Concerning Some Aspects of the Reaction between Urea and Cellulose

Southern Regional Research Laboratory [1]
New Orleans 19, Louisiana
June 27, 1961

To the Editor
Textile Research Journal

Dear Sir:

In his current letter to the Editor [p. 990], A. C. Nuessle makes two comments on our recent paper [4]. He first comments that we failed to acknowledge the contribution of D. D. Gagliardi, who carried out some early experiments with urea and cellulose as mentioned in Mr. Nuessle's early letter to us. Our reasons for citing Mr. Nuessle instead of Mr. Gagliardi are that we did not know with whom the ideas originated and we had communicated only with Mr. Nuessle. However, in his private communications with us, Mr. Nuessle did frequently mention work done by Mr. Gagliardi. These letters to the Editor then serve to credit Mr. D. D. Gagliardi with his part in the early work referred to in our paper as "Nuessle, A. C., private communications."

Mr. Nuessle's second comment is that we have given "misleading" emphasis to the use of aqueous urea solutions and that the reaction here occurs between cellulose and molten urea. It is true that we made extensive use of aqueous solutions, but our experimental conditions also include molten urea as well as biuret dissolved in dimethylformamide. Mr. Nuessle has apparently overlooked the part of our paper dealing with the latter and its relationship to the urea–cellulose system. The fact that our treatment of cellulose with biuret in dimethylformamide gave results indistinguishable from those obtained with aqueous urea solutions makes us doubt strongly that *urea* is the reactant. We will agree that urea is involved, as we showed in our paper, but not primarily. Comparison of our molten urea results with the data of Table I (first four conditions) of Mr. Nuessle's letter, indicates that our view is correct and that little reaction with cellulose has occurred in both cases. This is understandable as will also be pointed out shortly.

Before proceeding, we wish to state that one cannot disregard the likelihood of an acid-catalyzed reaction of cellulose with urea in hot aqueous solution (as with cupric chloride) where urea would, indeed, be the reactant. Benn and Jones [1] have obtained mono- and diglycosylureas by heating (70° C.) aqueous solutions containing aldohexoses (as well as aldopentoses), urea, and 5% sulfuric acid. Steyermark and co-workers [6] have made a more extensive study of the same reaction, varying temperature, catalyst, aldohexose, and solvent. We, too, have prepared and investigated glucosyl- and lactosylureas [5]. However, we did not consider that we had aqueous reaction conditions with our urea-treated celluloses since our wet samples were almost immediately dried by being placed directly into a forced-draft curing oven at temperatures of 140°, 155°, and 170° C.

The data given by Mr. Nuessle in Table I complement our published data very nicely. They support our conclusions regarding the reactant, as does his statement that "ammonia, a byproduct of the reaction, must also be removed in order to obtain a good reaction yield." The trend in the above-mentioned data in Table I can be explained easily if one considers not molten urea, but the products from the decomposition of heated urea. As it is stated in the literature, urea heated slightly above its melting point, 132° C. (or 270° F.) begins to decom-

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

pose, giving ammonia and cyanic acid [3, 7, 8]. This process is time and temperature dependent and as the temperature is raised, becomes very complicated and varied [2, 3]. Werner [8] and Malkina and Kazarnovskii [2] show that this is a reversible equilibrium process, and, therefore, in a closed system like the Parr bomb, the decomposition would be limited because the gaseous products cannot escape. In a curing oven, the ammonia would be removed rapidly, and the decomposition would proceed readily. The data of Redemann and co-workers [3] on biuret formation in molten urea at 140° C. (284° F.) show that when excess ammonia is present, less biuret is formed. This results, of course, from the equilibrium being shifted, whereby less cyanic acid is present to react further with urea to produce biuret. Cyanic acid is a quite reactive compound, and in our paper we have indicated some of its chemistry. Assuming that cyanic acid is the reactant, not only in the formation of biuret, but also in the formation of cellulose carbamate, then Mr. Nuessle's "much lower yield of Case 4 as compared to Case 5" is easily explained on the basis of the limited decomposition of urea in the Parr bomb. The low nitrogen contents we obtained using molten urea can be explained, not on the basis of lack of fiber penetration, but by the preferential reaction of the cyanic acid with the urea, which is present in very large excess. That our product from treatment with biuret was indistinguishable from those treated with urea follows readily when it is realized that heated biuret also decomposes to give cyanic acid [2]. The apparently less-than-anhydrous condition in Mr. Nuessle's Case 4 perhaps arises from concurrent formation of ammelide during the curing operation. Werner [8] states that biuret and cyanic acid react to produce ammelide and water, and under the conditions of drying and curing such a situation could arise.

In conclusion, we observe that all of the operations of drying and curing the urea-impregnated cellulose as carried out by Mr. Nuessle and ourselves lie close to or in the temperature range in which is found the rather involved scheme of decomposition for urea. Because of this and the above considerations, we are inclined to believe that the reaction which occurs when urea-impregnated cellulose is strongly heated does not involve molten urea, but rather cyanic acid, which is produced initially when urea decomposes.

Literature Cited

1. Benn, M. H. and Jones, A. S., *Chemistry & Industry* **1959**, 997 (1959).
2. Malkina, N. I. and Kazarnovskii, S. N., *Trudy Gor'-Kovsk Politekh. Inst.* **13**, No. 5, 32–36 (1957); through *Chem. Abstr.* **54**, 1538 (1960).
3. Redemann, C. E., Riesenfeld, F. C., and LaViola, F. S., *Ind. Eng. Chem.* **50**, 633–636 (1958).
4. Segal, L. and Eggerton, F. V., TEXTILE RESEARCH JOURNAL **31**, 460–471 (1961).
5. Segal, L., O'Connor, R. T., and Eggerton, F. V., *J. Am. Chem. Soc.* **82**, 2807–2811 (1960).
6. Steyermark, P. R., Steadman, T. R., and Germann, R. P., *Ind. Eng. Chem.* **53**, 212–214 (1961).
7. "Thorpe's Dictionary of Applied Chemistry," 4th ed., Vol. XI, London, Longmans, 1954, p. 797.
8. Werner, E. A., *J. Chem. Soc.* **103**, 2275–2282 (1913).

LEON SEGAL
F. V. EGGERTON

A Mechanical Model to Represent the Viscoelastic Properties of Polypropylene

Fabric Research Laboratories
Dedham, Mass.
July 5, 1961

To the Editor
Textile Research Journal

Dear Sir:

Introduction

Increasing precision in the geometry of polymers as introduced by the studies of Ziegler and Natta has resulted in the preparation of isotactic polymers with outstanding mechanical properties when compared with the atactic materials. One of the most important results of this work has been the stereospecific polymerization of propylene gas to yield a powder-like polymer, melting at 175° C., which is suitable for melt spinning [6]. A 230-den. continuous-filament yarn prepared from isotactic polyproylene (obtained from Industrial Rayon Corporation) was subjected to stress–strain studies at extension rates from 20–3,000,000%/min. using a wide variety of testing machines available at Fabric Research Laboratories, Plas-Tech Equipment Corporation, and the National Bureau of Standards, as well as at the Quartermaster Research and Engineering Command. The yarn used had a crystallinity of 65% and an orientation of about 90%.

Experimental Results

The ultimate properties of isotactic polypropylene are very good; the strength increases from 5.7 g./den. at 20%/min. to 8.4 g./den. at 500,000%/min. and possibly to 9.6 g./den. at ballistic speeds. The drop in elongation for this increase in strain rate is not excessively severe over most of this range, changing from 38% at 20%/min. to 28% at 500,000%/min. At ballistic speeds, the drop in ultimate elongation may be more severe, resulting in a value of 12%. Based upon these stress–strain curves, the work to rupture of isotactic polypropylene is far in excess of any known textile fiber over a wide range of strain rates.

The viscoelastic properties were investigated by obtaining the stress and modulus values at the same strain but at different strain rates. This has been done for 2%, 6%, 12%, and 16% extension and the results plotted as stress in dynes/cm.^{2} vs. log time in Figure 1. These curves are in the form of conventional stress relaxation curves [5].

Discussion

Inspection of the curves in Figure 1 shows that there are two areas of relaxation associated with polypropylene. The first has a short relaxation time, τ_1, equal to 10^{-2} sec., while the other has a longer relaxation time, τ_2, beginning at about 10^2 sec. Two decades in the middle ($10^{-1.5} \rightarrow 10^{0.5}$) are flat with no time dependence exhibited. The shape of this curve suggested to the authors that the behavior of isotactic polypropylene, in the time range of these experiments, could be represented by a simple mechanical model with two springs and two dashpots. The model selected, two Maxwell units in parallel, is shown in Figure 2. The constants given are those for 6% extension, where a slightly lower τ_1 value seems justified from inspection of Figure 1. A theo-

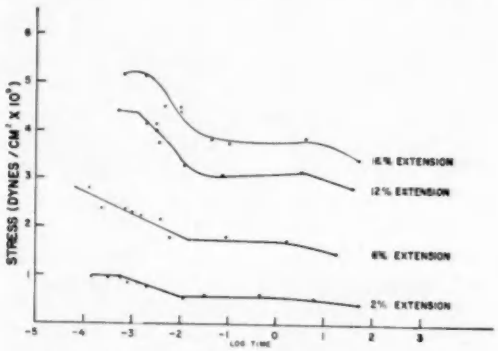


Fig. 1. Stress–log time plots in the form of stress relaxation curves.

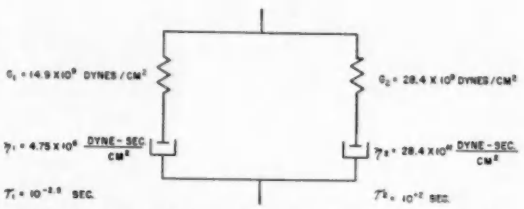


Fig. 2. Mechanical model used to represent isotactic polypropylene at 6% extension.

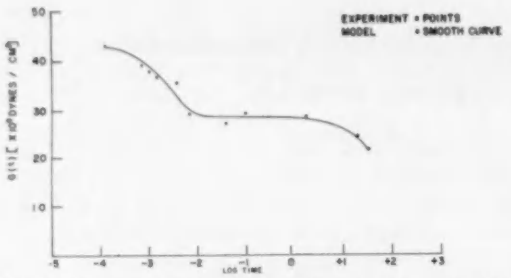


Fig. 3. Comparison of experimental data with mechanical model (6% extension).

retical modulus–log time curve can be constructed based upon this model by the use of the expression

$$G(t) = \frac{\sigma}{\epsilon} = G_1 e^{-t/\tau_1} + G_2 e^{-t/\tau_2}$$

where $G(t)$ is the modulus of the system, τ_1 and τ_2 are the relaxation times mentioned above, t is time, σ is stress, ϵ is the elongation, and G_1 and G_2 are the individual moduli of the springs in the model.

Substitution of various time values in this expression gives values from which the curve in Figure 3 is obtained. The points represent the experimental data at 6% extension. The agreement between the mechanical model and the actual behavior of isotactic polypropylene is quite apparent especially at the short-time range of the time spectrum. The second relaxation region might actually be a box distribution rather than a single relaxation time.

Hall has recently published data on the stress–strain properties of polypropylene [2]. The results are somewhat similar, showing two regions of maximum relaxation but perhaps a smaller region of no relaxation than the present authors found. Hall's data also indicate that the longer-time relaxation region might be better represented by a box distribution of relaxation times rather than by a single value of τ_2. Stress relaxation experiments by one of the present authors [3] substantiate the nearly linear behavior at long times.

It is interesting to calculate a value of the activation energy F^* associated with any relaxation time τ as suggested by Lyons [4]. Substitution of the value of τ_1 in the formula given

$$\tau = \frac{h}{2\pi^2 F^*} e^{F^*/kT}$$

where h is Planck's constant, k Boltzmann's constant, and T absolute temperature, yields for F^* a value of 18 kcal, indicative of molecular flow and the free volume effect. This is consistent with values obtained by Eyring et al. [1] for polyamide monofils, using forced vibration techniques.

Literature Cited

1. Eyring, H., Alder, M. C., Rossmassler, S. A., and Christensen, C. J., TEXTILE RESEARCH JOURNAL **22**, 223 (1952).
2. Hall, I. H., *Nature* **189**, 131 (1961).
3. Laible, R. C., unpublished work on the stress relaxation of isotactic polypropylene, 1961.
4. Lyons, W. J., *J. Appl. Phys.* **24**, 217–221 (1953).
5. Morgan, H. M., "Viscoelastic Behavior," in "High Speed Testing," Vol. 1, New York, Interscience Publishers, Inc., 1960, pp. 83–96.
6. Natta, G., *Chimica e Industria (Milan)* **47**, 647–652 (1959).

HENRY M. MORGAN
Fabric Research Laboratories
Dedham, Mass.

and

ROY C. LAIBLE
Textile, Clothing and Footwear Division
QM Research and Engineering Command
Natick, Mass.

An X-Ray Study of Partially Hydroxyethylated Cellulose

Physical Chemistry Division
Pulp and Paper Research Institute of Canada
McGill University, Montreal
July 10, 1961

To the Editor
Textile Research Journal

Dear Sir:

This note deals with an X-ray study of hydroxyethyl cellulose carried out to obtain some information about the course of the reaction between ethylene oxide and alkali cellulose. Specifically it was of interest to find out whether at low degrees of conversion this reaction is intracrystalline or confined solely to the so-called "amorphous" regions. This question has an important bearing on the uniformity of substitution, which in turn determines the solubility behavior and other properties of the derivatives.

The X-ray diffraction photographs were made with a Seifert unit, using a flat-film camera which has been described elsewhere [5]. The sample–film distance was 5.5 cm. The radiation used was nickel-filtered CuK_α and the X-ray tube was operated at 30 kv, 20 ma. Exposures were made on Kodak type F double coated X-ray film and were 2 hr. in duration. Some representative photographs are shown in Figure 1. Measurements were made on seven samples of hydroxyethyl cellulose and one sample of a regenerated alkali cellulose which served as a reference standard. The samples of hydroxyethyl cellulose were prepared by treatment of alkali cellulose with ethylene oxide. All the samples were prepared from a Spruce sulfite pulp having an alpha content of 90.6% and a Tappi viscosity of 20 cp. (1% cuprammonium solution). The ethylene oxide content of the samples is characterized by the degree of substitution (DS) which in the present case signifies the total number of ethylene oxide molecules per anhydroglucose unit, independent of whether they form polyglycol chains or not. Values of the DS for the various samples are given in Table I.

Examination of the X-ray photographs (Figure 1) and the corresponding radial photometer curves (Figure 2) shows that as the reaction proceeds the innermost arc, the (101), A_0 of cellulose II, becomes stronger in intensity and decreases in diameter. At the higher values of DS (greater than 0.68) it becomes a broad diffuse halo. There is no significant change in the position and intensity of the $(10\bar{1})$, A_3 interference. In addition the A_4 and III_1 reflections, corresponding to (002) and (031) (130) respectively, are almost completely missing in the samples of DS 0.68 and greater.

Interplanar spacings, d, calculated from comparator measurements on the X-ray photographs are given in Table I. The experimental values obtained for the regenerated alkali cellulose show fairly close agreement with the accepted values for cellulose II, thus giving confidence in its use as a control. It is clear that the most striking change in the lattice takes place in the spacing between the (101) planes. As seen in Figure 3 there is a gradual increase in the spacing of the (101) planes from 7.2 Å in the control sample of cellulose II to 10.0 Å in the hydroxyethyl cellulose of DS 0.68.

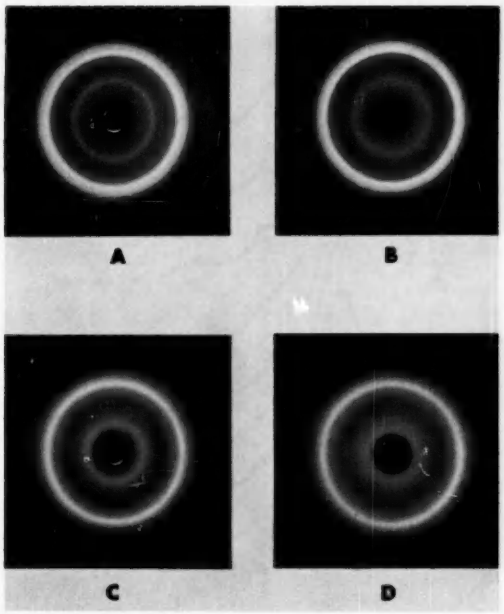


Fig. 1. X-ray diffraction photographs of cellulose II and partially hydroxyethylated wood cellulose. Nickel-filtered CuK_α radiation; sample-to-film distance 5.5 cm.; A, cellulose II; B, C, and D, partially hydroxyethylated cellulose of DS 0.22, 0.94, and 1.78, respectively.

TABLE I. Interplanar Spacings for Partially Hydroxyethylated Cellulose and Regenerated Cellulose

Spot	Plane	Regenerated cellulose d(Å)	Hydroxyethyl cellulose DS 0.22 d(Å)	DS 0.32 d(Å)	DS 0.68 d(Å)	DS 0.94 d(Å)	DS 1.24 d(Å)	DS 1.56 d(Å)	DS 1.78 d(Å)
A_0	(101)	7.26	7.96	8.1	10.0	9.7	dh*	dh*	dh*
A_2	(10$\bar{1}$)	4.46	4.50	4.50	4.50	4.2	4.1	4.1	4.0
A_4	(002)	4.08	4.20	4.20	—	—	—	—	—
III_1	(031)(130)	3.14	3.20	3.20	—	—	—	—	—

* dh = diffuse halo.

The gradual increase in the (101) spacing during the introduction of hydroxyethyl groups into the crystal lattice of alkali cellulose is comparable with the lattice change which occurs when native cellulose is treated with certain swelling agents [1, 4, 6]. The effect has also been observed in the partial acetylation and benzylation of cellulose [2, 7]. The explanation is the same in all cases; the substituent groups or molecules of swelling agent force the anhydroglucose units apart so that the distance between the chains is increased. The susceptibility of the (101) planes to attack by the ethylene oxide may be ascribed to the fact that they are very rich in hydroxyl groups, which are presumed to be oriented perpendicular to the planes. Under conditions where hydrogen bonds are broken, such as exist in alkali cellulose, the (101) planes would therefore be planes of weakness and might indeed be looked upon as cleavage planes [8].

The distension of the lattice as well as the other changes indicated above show that the crystallites are attacked to a certain extent in all the samples. The results suggest further that the reaction is intercrystalline as well as intracrystalline from its very start. It is presumed, however, that the rate of

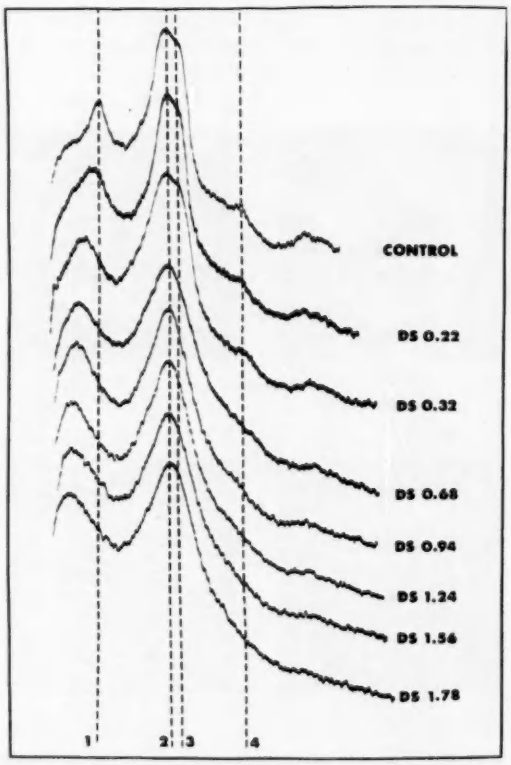


Fig. 2. Radial photometer tracings for partially hydroxyethylated celluloses. The dotted lines (1–4) show respectively the positions of the interferences 101, 10$\bar{1}$, 002 and (031)(130) of the cellulose regenerated from alkali cellulose.

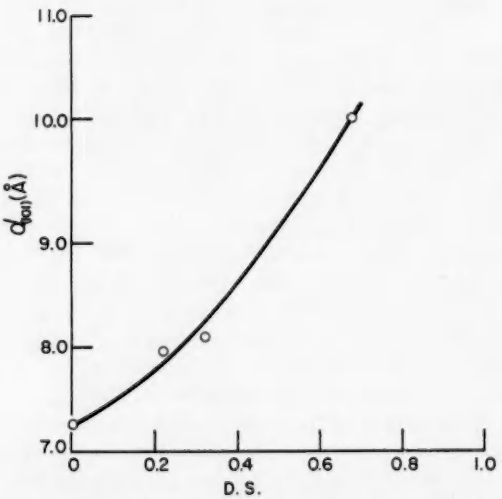


Fig. 3. Plot of the (101) interplanar spacing as a function of the degree of substitution.

conversion would be somewhat greater in the amorphous regions.

Since the reaction is intracrystalline it follows that the distribution of the substituent must be fairly uniform. The results obtained in this investigation are in agreement with the findings of Croon and Lindberg [3] who, in studying the distribution of the substituents in similar hydroxyethyl celluloses, found that all the glucose residues in alkali cellulose seemed to have almost the same accessibility.

Acknowledgments

The author wishes to thank Dr. Ingnan Jullander of Mo och Domsjö Aktiebolag, Örnsköldsvik, Sweden, for his interest in this work and for kindly supplying the samples used. Thanks are also due to Dr. I. Croon for many helpful discussions.

Literature Cited

1. Creeley, J. J., Segal, L., and Loeb, L., *J. Polymer Sci.* **36**, 205 (1959).
2. Creeley, J. J., Stanonis, D. J., and Klein, E., *J. Polymer Sci.* **37**, 43 (1959).
3. Croon, I. and Lindberg, B., *Svensk Papperstidn.* **59**, 794 (1956).
4. Davis, W. E., Barry, A. J., Peterson, F. C., and King, A. J., *J. Am. Chem. Soc.* **65**, 1294 (1943).
5 Ruck, H., Kouris, M., and Manley, R. St. John, *J. Ultrastructure Research* **3**, 46 (1959).
6. Sisson, W. A. and Saner, W. R., *J. Phys. Chem.* **43**, 687 (1939).
7. Vermaas, D., Hermans, P. H., and Weidinger, A., *J. Polymer Sci.* **2**, 406 (1947).
8. Woods, H. J., in J. Honeyman, "Recent Advances in the Chemistry of Cellulose and Starch," London, Heywood and Co. Ltd., 1959, p. 144.

R. ST. JOHN MANLEY

Information for Contributors

Subject Matter

There are five principal classes of contributions suitable for the JOURNAL: (1) fundamental research articles, presenting important new information and data in any area of science related to the textile field; (2) technical papers describing development work, engineering advances, and innovations in manufacture and processing; (3) laboratory techniques with sufficient experimental data to illustrate the utility of methods or equipment described; (4) Letters to the Editor, seldom exceeding 1000 words, which are intended for prompt publication of new discoveries or observations, or for informative comment on papers previously published in the JOURNAL; (5) review articles of an authoritative and critical nature on a topic of major importance.

With the exception of Letters to the Editor, all submitted manuscripts are sent to qualified persons for review and critical comment. The names of reviewers are not disclosed without their consent.

Preparation of Manuscripts

Arrangement—Any logical arrangement of the subject matter is acceptable.

Style—The JOURNAL's style guides are "Webster's Unabridged Dictionary" and the "Government Printing Office Style Manual."

Authors' Names and Affiliations—This information should be given exactly as it is to appear in print. If the author is no longer with the company where the work was done, his new affiliation should be given in a footnote.

Typing—Manuscripts should be typed, *double-spaced; two copies must be submitted.*

Abstract—A brief abstract (about 150 words) should accompany each paper.

Equations and Formulas—Equations are numbered in parentheses to the right; they are referred to in the text as Equation 2, Equation 11a, etc. (no parentheses). All equations should be checked carefully by the author to avoid costly alterations which require hand-setting of type. Exponents and subscripts should be legible and properly positioned. There should be a clear distinction between small and capital letters, between 1 (one) and l (el), and between the letter O and zero. Fairly simple structural formulas can be set in type; complicated ones should be lettered in *India ink* on a separate sheet of paper, from which a plate will be made. Greek letters should be written clearly; it is helpful to spell out the name of an unfamiliar symbol in the margin.

Illustrations—Drawings and graphs should be in *India ink* on white paper or blue tracing cloth, or clear glossy photographic prints of such drawings. Engravings cannot be made of drawings in blue ink. It is essential that all lines be strong and solid; when the drawing is reduced the lines become thinner and discontinuities are accentuated. Lettering must be large enough to accommodate reduction; the following guide will be helpful:

Size of Original	Height of Letters
4 × 5	2–3 mm.
8 × 10	4–5 mm.
10 × 16	8+ mm.

Titles should not appear on the drawings; they will be set in type below the figures and should be submitted together on a separate sheet. Any legible reproduction of the figures may accompany the second copy of the manuscript.

Photographs—Photographs should be glossy prints, clear, sharp, and with as much contrast as possible without loss of detail. Identification of the figures should be made very lightly on the back with a soft pencil.

Literature Cited—All references cited in the text should be given in brackets, e.g., [2] by numerals corresponding to a numbered list, *arranged alphabetically by author,* at the end of the paper. The information should be given in the following order: authors' names, initials, name of publication, volume number, (place of publication and publisher for a book), inclusive page numbers, and year of publication. Abbreviations of journal titles follow those used by *Chemical Abstracts.*

In the December Issue

A Study of the Interaction between 2-Thiobarbituric Acid and Cotton. *L. Rebenfeld*

The Relation of Skein Dimensions to Strength and Yarn Number Measurements. *D. S. Hamby, E. B. Grover, W. C. Stuckey, and M. Shaikh*

The Effect of pH and Detergents on the Felting of Shrink-Resistant Wool. *J. R. McPhee and H. D. Feldtman*

Fiber Configuration in Sliver and Roving and its Effect on Yarn Quality. *A. R. Garde, V. A. Wakankar, and S. N. Bhaduri*

Tensile Behavior of Cut Skeins and Single Threads. *T. Radhakrishnan and B. R. Shelat*

The Kinetics of the Absorption and Desorption of Single Ions by Keratin Fibers. *Donald L. Underwood and Howard J. White, Jr.*

A Modification of the Method for Defining and Measuring Crimp of Textile Fibers. *M. Shiloh, J. Goldstein, D. Mejzler, and E. Alexander*

Shrink-Resist Treatment and Laundering of Wool Fabrics. *J. R. McPhee*

Boundary Friction of Textile Fibers. *Tomlinson Fort, Jr. and J. S. Olsen*

Studies on High Fastness to Light in Coloring Matters in Hydrophobic Substrates. Disperse Dyes in Cellulose Acetates and Polyesters. *Charles H. Giles and Syed M. K. Rahman*